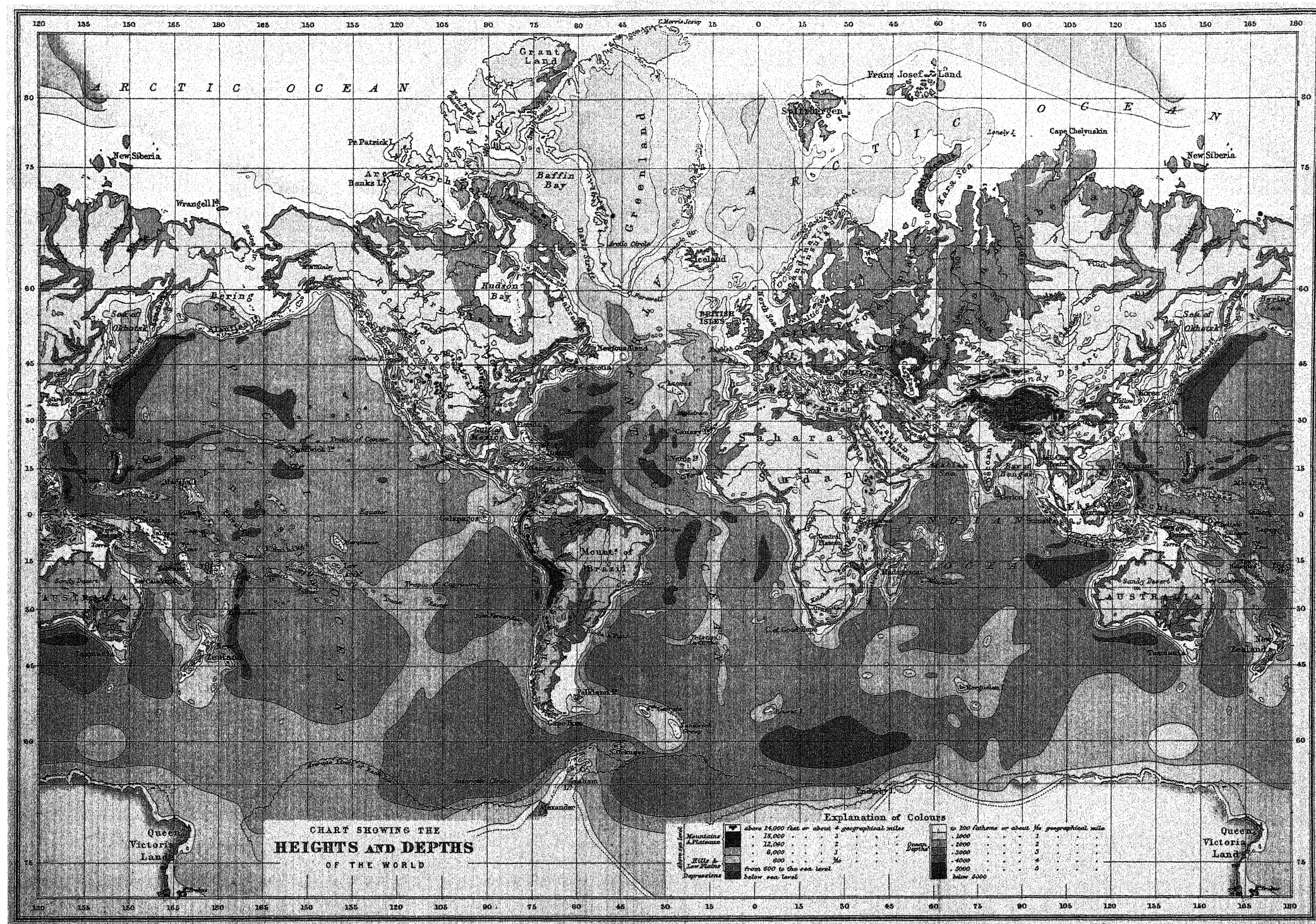


SCIENCE  
IN MODERN LIFE











# SCIENCE IN · MODERN · LIFE

A SURVEY OF SCIENTIFIC DEVELOPMENT  
DISCOVERY AND INVENTION AND THEIR  
RELATIONS TO HUMAN PROGRESS AND  
INDUSTRY

PREPARED UNDER THE EDITORSHIP OF

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# GEOLOGY

(Continued)

## CHAPTER XI

### TERTIARY CLIMATE. THE GREAT ICE AGE. MODERN GEOGRAPHY. DEVELOPMENT OF THE HUMAN RACE

#### CLIMATE OF THE TERTIARY PERIOD

The evidence of the plants obtained from the Eocene and Oligocene sediments of many areas points conclusively to a sub-tropical climate over northern and central Europe. Figs, palms, and magnolias seem to have been characteristic of as high latitudes as Greenland, which is now occupied by ice nearly to the coast all the year round, whilst the limit of trees is several degrees farther south. Similar conditions prevailed during the early Miocene, but a change to a cooler climate set in later, for the palms and several of their associates disappeared from northern latitudes, and the general character of the vegetation of those regions resembled in many respects that of the present day. The earth movements of the Miocene and early Pliocene seem to have hastened the cooling. The gradual introduction of Arctic elements into the vegetation of a temperate area, already referred to in the case of the English Pliocene deposits, has been observed generally throughout Europe and North America at this time. The warm climate of the above regions during the early Tertiary period becomes more remarkable in view of the fact that the contemporaneous vegetation of Japan, Kamchatka, and other places in north-east Asia bordering the Pacific points to a considerably cooler temperature than exists to-day. As Greenland and Japan lie on opposite sides of the pole the hypothesis was put forward that the pole has shifted since that period. There are

many difficulties, however, in accepting such an hypothesis and the explanation must be sought for in another direction.

### THE GREAT ICE AGE

The general lowering of temperature which took place over what may be called the Atlantic region of the Northern Hemisphere foreshadowed an episode of considerable importance, viz. the great advance of thick masses of ice from North Polar areas to low latitudes. The glacial epoch or "Great Ice Age" as it is called, was the last important influence in shaping the surface features of the earth. Those were not markedly different from the present, since as a rule subsequent changes of level have been comparatively small.

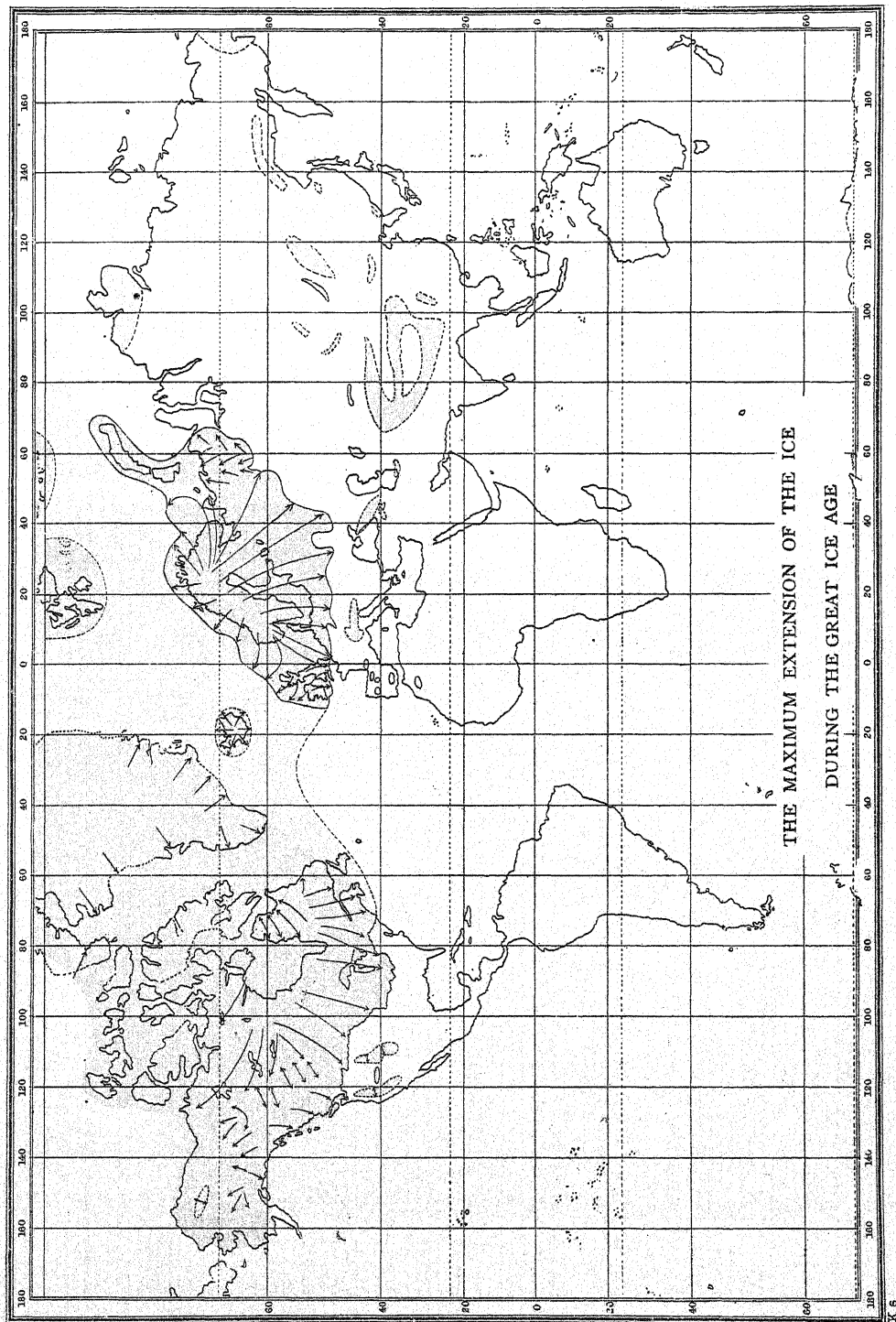
**CONTORTED DRIFT.**—On the east coast of England the latest Pliocene deposits are succeeded directly by others which are of glacial origin. One of the most remarkable is the **CONTORTED DRIFT**, about which much difference of opinion still exists. It has been compared with certain deposits found around the margins of the ice in Greenland and Spitzbergen at the present day, and its peculiar disturbed character is attributed to the crushing and shearing of the ice, and its included frozen material as it was forced on to the land from the direction of the North Sea.

It is succeeded by the **GREAT CHALKY BOULDER CLAY**, which covers an enormous area in the east of England, and is supposed to have been formed at the same time as the extensive sheets of clay with boulders occurring in other parts of the British Isles. It is only in the east of England, however, that its relation to the Pliocene deposits is shown; elsewhere it rests quite unconformably on older rocks.

The general features of a glacial period have been indicated when describing the modern work of ice in an earlier chapter, but the examination of the characteristic deposits is obviously facilitated when the ice has receded from the area, and accordingly a great part of our knowledge of the processes of glaciation has been derived from a study of regions where those processes have passed away. The glaciation of the Great Ice Age differs from that of high latitudes at the present day in its enormously greater extent, of which a better idea can be gleaned from the map than from a verbal description (see plate). Attention may be called to a few points of importance.

**DISTRIBUTION OF THE ICE-SHEETS.**—It will be observed that the Irish Channel and the North Sea as far as the Straits of Dover were entirely occupied by an ice-sheet during the maximum glaciation. The





The shaded portions show the areas which were covered by ice. The lighter shading indicates uncertainty. The direction in which the ice moved is shown by the arrows. (Eurasia after James Geikie, N. America after Chamberlin and Salisbury.)





margin across the south of England may be defined approximately by a line drawn from the neighbourhood of London to the Bristol Channel, and it must have lain quite near the present coast of South Wales, while the south of Ireland was strongly glaciated.

The southern margin in North America reached lower latitudes than in Europe. In the Mississippi valley its farthest lobes were at about the latitude of the south of Spain and Sicily.

DIRECTIONS OF ICE MOVEMENT.—As the directions of the arrows

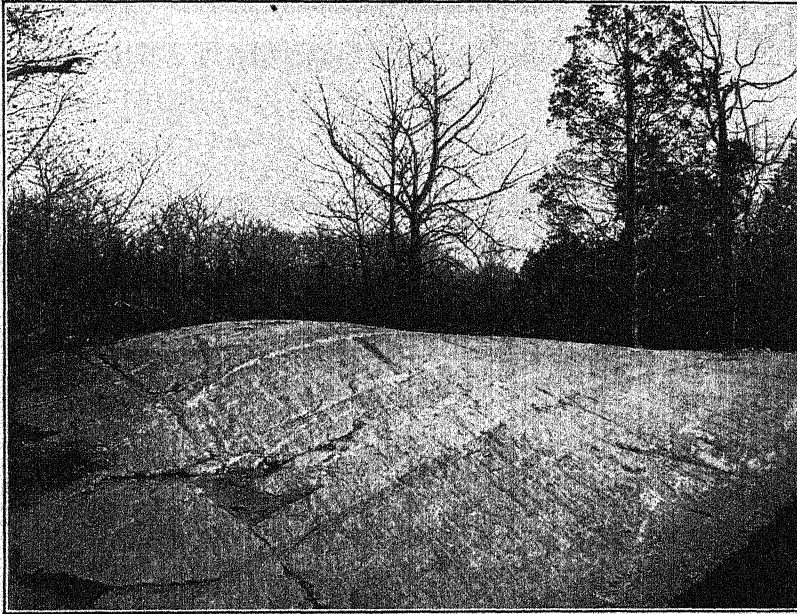


Fig. 40.—A Polished Surface of Rock (Roche Moutonnée) in Bronx Park, N.Y. (Willis)

indicate, the ice did not move out from one but from many centres, which did not necessarily coincide with the highest points of land, though some effect must be attributed to them. This is especially remarkable in North America, where one of the centres lay over the low, flat area surrounding Hudson Bay, whence the ice spread for nearly 1000 miles towards the rising ground of the west. Evidence of a similar kind, but on a smaller scale, has been obtained in Europe. The movement seems to have been determined to a great extent by the precipitation or snowfall, for in Scotland the ice radiated, not from Ben Nevis, but from a lower point which roughly coincides with the maximum rainfall at the present day.

It will be noticed also that isolated areas carried glaciers which have

since disappeared or have dwindled in importance. Most of the modern Alpine glaciers (using this term in its wide sense) are but relics of much larger ones which formerly occupied those regions.

RESULTS OF THE ICE AGE.—The Great Ice Age has left abundant traces behind it. The rocks over which the ice moved have been thoroughly grooved, scratched, and polished (fig. 40), thus giving to the

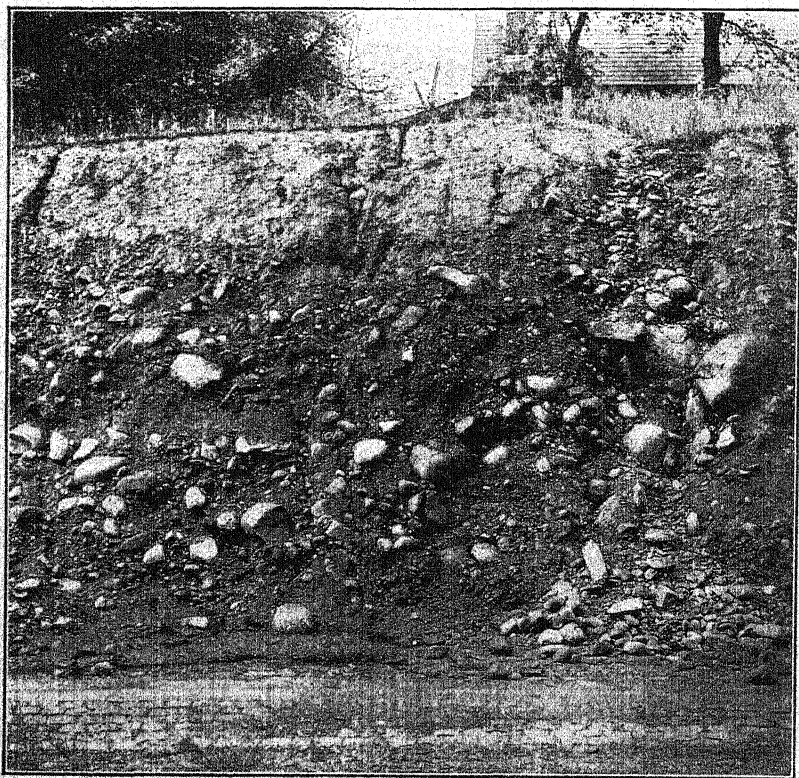


Fig. 41.—A Section of Boulder Clay (after Chamberlin and Salisbury)

region a smooth undulating aspect when viewed in the direction of ice movement, but a more rugged appearance when viewed from the opposite direction. But of greater importance are the deposits, which are often of considerable thickness, and have contributed not a little to influence the scenery of certain districts. Various kinds may be distinguished.

1. MORaine MATERIALS borne in, on, or under the ice, which were left on the surface when the ice disappeared. They consist as a rule of clay or sand in which are embedded angular or partially rounded blocks of various sizes (see fig. 41), many of them showing characteristic striation



and polishing. Valley glaciers usually left long lines or crescentic ridges of morainic material, but an ice-sheet gave rise to a more or less regular cover which tends to mask the pre-existing land features by filling up the hollows. Those districts where the deposit occurs in force are distinguished by numerous shallow pools and lakes scattered about on its uneven surface; many of these have been filled up by the growth of mosses and other vegetation and are now represented by peat flats.

Blocks of rock, often of large size, known as ERRATICS may be found in most glaciated regions; they were probably carried on the surface of the ice, and in some cases are known to have travelled hundreds of miles; on the recession of the ice they were frequently left stranded in apparently tottering positions on hill and mountain sides, and occasionally on rock pinnacles, whence they derive their name of *blocs perchés*. A granite boulder from the Alps, probably weighing about 15,000 tons, lies nearly 1000 ft. above the Lake of Neuchâtel in Switzerland. Such a mass is equivalent to a cube of rock of 20 yd. a side. The distribution of erratics of known origin furnishes one of the means of determining the direction of movement of the ice which carried them.

2. FLUVIO-GLACIAL MATERIAL, which usually consists of stratified sand and gravel, bearing distinct evidence of having been sorted by the action of running water. Wide sheets of such deposits fringed the margin of the ice sheet, especially where it remained stationary for a considerable time; they are sometimes theoretically distinguished from those formed within the region actually covered by the ice, though such a distinction is far from easy in practice. In some districts they form elongated mounds, or DRUMLINS, arranged with their long axes in the direction of ice motion, while in others long ridges of stratified deposits wind about on the surface without any relation to present hills and valleys, and the suggestion has been put forward that they are the deposits of streams which flowed within the ice. The figure (fig. 42) shows the distribution of such ridges or *åsar* crossing the heights and hollows around Lake Mälär near Stockholm; they strongly recall the ramifications of a drainage system.

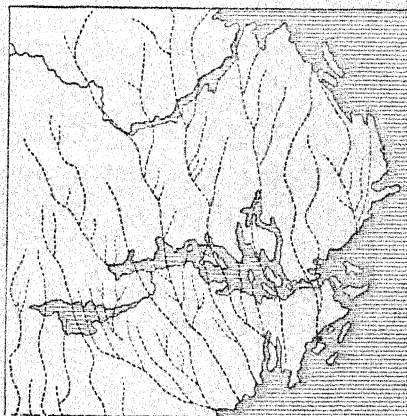


Fig. 42.—Gravel Ridges (*Åsar*) around Lake Mälär, Sweden (after Törnebohm)

3. GLACIAL MARINE DEPOSITS.—It was supposed at one time that the boulder-clays, sands, and gravels of glacial origin were deposited in the sea by icebergs derived from ice in higher latitudes, and therefore indicated changes of level of several hundreds of feet. This view is no longer generally held, and proof is wanting of the existence of any such deposits of Pleistocene age. The fact that patches of sand and gravel containing abundance of marine shells occur at great altitudes in several parts of Britain were thought to furnish decisive evidence that those deposits were formed under the sea.

Recent study has shown, however, that they were probably carried up to their present positions by the ice which had ploughed its way along the sea bottom and picked up the sediments with their included shells. It has been observed that these marine remains always occur at those places where the ice is known to have impinged on the coast from the direction of the sea, and that the shells of species which inhabit different depths are all crowded together. The fact that some of these deposits occur at heights of 1200 ft. or more show how great must have been the pressure which forced them up to such heights. The chief localities are Moel Tryfaen in Carnarvonshire, various places in Cheshire, and on the north-east coast of England.

INFLUENCE ON DRAINAGE.—It is necessary to say a few words about the influence of the glacial episode on the lines of drainage which had been established, and had in many cases reached fairly mature stages before its advent. Many small lakes, and not a few large ones, owe their origin to barriers of glacial deposits blocking up their outlets; others must have existed which have worn down a channel through the incoherent material, and regained their former courses at the bottom of the valley. Traces of such lakes have often been detected by lines or terraces of accumulations along their margins. Evidence has been obtained of former temporary lakes which were dammed up by a barrier of ice across the lower part of the valley, and it is claimed that the terraces which occur at various levels near Glenroy in Scotland, and known as the Parallel Roads, mark successive levels of overflow of such ice-barred lakes. Several lakes of glacial origin now flow in a channel of solid rock, and largely owe their permanence to this fact. Another characteristic effect of ice occupation was the diversion which many of the smaller rivers suffered.

During the glacial period the functions of the lines of drainage were suspended, and after the recession of the ice the streams began to flow in most cases over an accumulation of glacial material, the solid rocks being only reached after this had been cut through. A channel started in the



hard rocks tended to be permanent, and the stream was therefore prevented from regaining its former bed. Frequent cases are known where a stream appears to forsake a wide valley, where it might be expected to flow, and to force a passage through a narrow gorge with precipitous sides cut in the solid rocks. They usually denote a diversion during or immediately following the glacial period. There are other examples of streams which have been suddenly rejuvenated by glacial diversion, whereby they acquire a more rapid fall or gradient, and consequently are enabled to deepen their channels. If the valley was a mature one before the diversion, the stream had numerous windings or meanders, which persisted during the renewed cutting down, giving rise to tortuous gorges.

ADVANCE AND RECESSION.—It is claimed by many investigators of the Great Ice Age that there is evidence of repeated advance and recession of the glaciers or ice-sheet, which are usually attributed to alternate phases of severe and mild climate, though they might equally well have followed increased or diminished precipitation. Accordingly they distinguish several glacial and interglacial conditions between the first advance and the final recession of the ice. The American deposits are thought to furnish evidence of six distinct periods of advance, separated by recession of the ice and the growth of vegetation on the area vacated by it. It is stated that some of these interglacial stages must have been of considerable duration, probably greater than the interval between the last retreat of the ice and the present day. As a rule, they are characterized by deposits of stratified sand and gravel, laid down by streams flowing from ice in higher latitudes. There was also erosion and redeposition of the products of the preceding glaciation. The next advance of the ice disturbed and frequently ploughed up the earlier-formed materials, which were assimilated in the fresh deposits. These are the chief lines of evidence relied on in distinguishing the various stages. It is considered also that the vegetation of the interglacial stages indicates a mild climate, in some cases not differing sensibly from that of the present day.

Similarly in Europe certain glacialists favour the view that there were six glacial stages, separated by five interglacial stages; others, notably in Germany, would reduce the number of the former to three, which accords favourably with what is known of the English deposits. Thus there are still many outstanding differences of opinion among those who have devoted much time to the study of the complicated events of the period.

CAUSES OF THE ICE AGE.—For an account of the older theories of the cause of the glacial period the reader is referred to various text-books and manuals on general geology and on the Ice Age in particular. An attempt will be made here to indicate the main lines of the new theory of Chamberlin and Salisbury, both on account of its plausibility and the many points of interest which it raises. In the discussion of the Permian glaciation the influence of earth movement and upheaval on the climate of the succeeding period was briefly outlined. Inasmuch as the Pleistocene glaciation also followed intense disturbance of the earth's crust, it stands on the same footing, and therefore it is presumed that from that cause alone the general temperature would fall. There is this difference, however; the earlier glaciation prevailed over low latitudes (*i.e.* approaching the Equator), while the later spread out from the poles, and therefore a smaller change of temperature would suffice to bring it about. The localization of the glaciation, and the causes which would bring about a diminution of the amount of carbon dioxide and water vapour in the air, are the problems that this hypothesis seeks to solve.

As a special cause for the changes of temperature during the Tertiary period, considerable importance is attached to the deep-seated circulation of the oceanic waters. To begin with the warm climate that preceded the glacial period; near the Equator evaporation was rapid, and hence the salinity of the water increased. This made the sea water heavier, and although the high temperature acted in the opposite direction, it is considered that the increase in weight, due to increased salinity, more than counterbalanced the effect of the high temperature.

The warm salt water, therefore, sank to the depths and spread towards the poles, and, rising there, ensured a mild climate to those regions. Near the Equator the sea water absorbed as much carbon dioxide as it could hold at the temperature, and carried it down to the depths; but near the poles, where the temperature was lower, the water could hold more, and therefore the warm water from the Equatorial regions which rose there, being undercharged with that gas, immediately began to absorb it from the atmosphere, whereby its effect in stopping loss of heat by radiation diminished, and the surface temperature of the earth consequently fell. As this process continued, freezing began to take place in the high latitudes, and, as will be shown, a reverse change then set in. On being converted into ice, the sea water discharged its gases and salt, and the layer immediately under the ice became increasingly saline, and began to sink, displacing the warm water previously rising there. After a time the cold



water from the polar regions filled the depths of the ocean, and then began to rise in the warmer regions.

The conditions for carbon-dioxide circulation were then reversed. That gas was absorbed by the water at a low temperature, and when freezing occurred, an additional quantity was set free. The cold water descending from underneath the ice layer was therefore highly overcharged, and in virtue of this and the higher temperature a great discharge into the atmosphere took place, when the polar current rose in the Equatorial regions. Loss of heat by radiation then diminished, and the general temperature steadily rose, until melting occurred in the polar regions, when the change towards a cooler climate would be ready to begin once more. Thus alternations of warm and cold conditions might follow one another until the general influences, due to earth movement, ceased to be operative.

In the theory a large number of subsidiary effects are dealt with, but to avoid complicating the statement they are not introduced here. From analogy they suggest that the localization of the Pleistocene glaciation was determined by the distribution of the areas of low barometric pressure, for the present glaciations of Greenland and Alaska nearly coincide with these areas in the Northern Hemisphere. Further, there seems to be some relation between the limits of the great ice-sheet and the track of storms across the Atlantic at the present day.

It is probable, therefore, that these meteorological features were in existence prior to the glacial epoch, and that they exerted some influence upon the distribution of the glaciation. The areas of low and high pressure are probably connected, in some way not fully understood, with the present configuration of the land and sea.

**STEPPE PERIOD—LOESS.**—A peculiar deposit of widespread occurrence in Eurasia and North America must be mentioned here, because though not directly of glacial formation, it is closely connected with that episode. This is the loess, and is usually regarded as being of later date than the glacial deposits, but American geologists claim that it was formed in part contemporaneously with them and in part later.

It is a fine, powdery deposit of a brownish-grey colour, typically showing no stratification, but traversed by numerous vertical and branching tubes, which give it a tendency to break in their direction (fig. 43). It contains minute angular fragments of undecomposed minerals, as well as appreciable quantities of calcium carbonate and oxides of iron. These latter tend to form concretions of various sizes, which often stand out in fantastic shapes on weathered faces, suggesting the names "loess

mannikins" and "loess dolls" frequently applied to them. Bones of animals and land shells are embedded in it, which strongly suggest a terrestrial origin.

Its distribution is highly peculiar; it occurs on the hills and in the valleys, and often reaches in Europe to altitudes of 1500 ft. or over. The thickness varies greatly in different parts, being greater in the valleys, and generally tailing away on the hills. Most commonly it tends to cover one side of a valley, and to be absent from the other; the covered side being that protected from the prevailing wind. Where it comes in contact

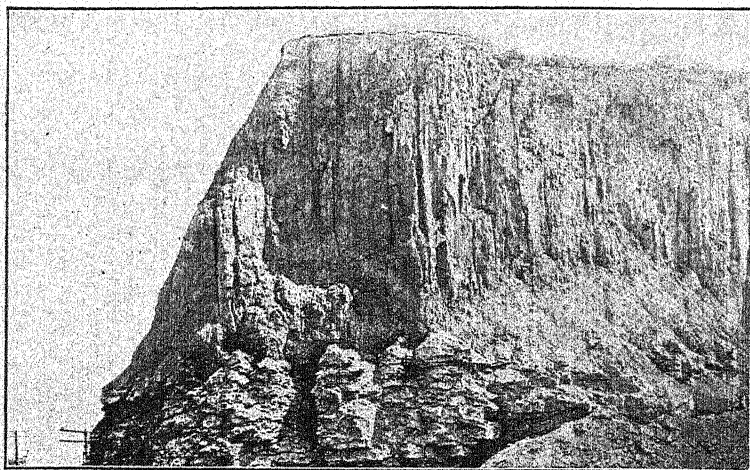


Fig. 43.—A Section of the Loess at Kansas City, showing its columnar structure (after Chamberlin and Salisbury)

with the hill slopes it usually contains seams of pebbles or angular fragments, but the bulk of the deposit is singularly uniform and free from coarse material. It has a wide distribution over central Europe, around the old crystalline masses, and in the south-east, in Hungary, Roumania, and other places. Strangely enough it does not occur in Russia or in the Baltic region.

It is in China, however, that the loess attains its grandest development. It is often found at altitudes of over 10,000 ft., and in the basin of the Hoang-Ho reaches a thickness of more than 1000 ft. Ravines with precipitous walls have been cut through the deposit from summit to base, and its uniformity and the absence of stratification throughout such a great thickness are very striking. When it occurs on a fairly level plateau it forms a more or less uniform cover; but in a hilly country it fills the hollows between the heights, and its surface is then observed to present a characteristic concave curve, somewhat resembling that formed by a



chain suspended by the ends (catenary curve). Various suggestions have been offered as to its mode of origin, but it is now generally agreed that the greater part is not a fluvatile deposit.

Baron von Richthofen was led by his investigations on the loess of China to attribute its accumulation to the action of wind in an arid region of steppe character, for he observed that on the plains of Asia deposits of a similar kind were then in process of formation. Those regions are visited, at intervals, by violent storms of dust, which completely obscure the sun from view for several days. If this dust falls on a steppe region, it is protected from the wind by the vegetation, and remains where it falls. The plants and grasses continue to grow up through the layer of dust, and are ready to act in a similar manner when the next storm occurs, and thus a great thickness may in time accumulate. He supposes, therefore, that the retreat of the ice was followed by cold, dry climatic conditions, during which the fine material left in enormous quantities on the surface of the land by the glaciers, and which was unprotected by a growth of vegetation, would be readily picked up by the wind, and after being carried often to great distances, deposited in regions where a vegetation of steppe character prevailed.

This theory certainly accounts for most of its peculiarities of distribution, as well as its physical characters. The angular nature of its minute particles accords well with a derivation from glacial material, while the curious ramifying tubules, so universally present, are supposed to be the hollows left by the decay of the rootlets and stems of the plants which retained the dust deposited among them. After it was formulated, this view received unexpected confirmation from a study of the loess organic remains. The shells were previously known to be those of land or amphibious animals, but the bones and other remains showed that the animals were mostly of the same species as those which inhabit the steppes at the present day. The bones of extinct elephants, found commonly towards the base of the loess, occur in other regions where that deposit is absent, notably in cave debris and other accumulations in Britain and elsewhere.

The insular position of the British Isles probably ensured a fairly moist climate during that period, and hence true loess could not be formed though various accumulations in the southern counties are probably contemporaneous with it.

FOREST PERIOD.—A change to a milder, moister climate brought steppe conditions to a close in central Europe, and allowed a more luxuriant vegetation to flourish. A forest growth appeared over wide



regions, and the Forest period, as this has been called, persists to the present day, though the forests themselves are fast disappearing through the agency of man.

ORIGIN OF MAN—OLDER STONE (PALÆOLITHIC) AGE.—The date and manner of appearance of the human race have long occupied the minds of geologists and archæologists, but the problem is still far from settled. There is definite evidence of the existence of man during the Steppe period; for PALÆOLITHS or stone implements of warfare and of the chase are preserved in abundance in certain deposits, and are associated with the remains of animals which are found also in the loess. These implements, though crude, yet display considerable ingenuity and mechanical skill, and forbid the supposition that they were those of the earliest human beings. There is therefore a strong probability, almost amounting to certainty, that man must have existed *somewhere* prior to the Steppe period, *i.e.* during or before the Great Ice Age, but whether in the region visited by the ice or in some other remains unsolved, for although the discovery has been repeatedly announced of human relics in preglacial or interglacial deposits, a careful examination of the evidence has always shown that the true age of those deposits could not be conclusively proved. It has also been claimed that stone implements of a still earlier type (EOLITHS) occur in certain areas, but the difficulty with most of these is to prove that they were implements at all, and not merely naturally formed lumps of stone which bear a fancied resemblance to such.

NEWER STONE (NEOLITHIC) AGE.—The man of the Forest period had attained great skill in the shaping and finishing of his implements, and the manufacture of arrowheads, spearheads, knives, &c., of flint must have occupied not a little of his time. They are known as NEOLITHS, and are characterized either by elaborate chipping or by ground edges and smooth polished surfaces.

BRONZE AND IRON AGES.—At a later date came the discovery and use of metals, which gradually replaced stone for the manufacture of implements, though the two were used side by side for a time, as is shown by imitations of metal weapons in stone. It is a curious fact that the application of bronze preceded by a long interval that of iron, and hence various stages can be distinguished, such as the Bronze Age, the Prehistoric Iron Age, and the Historic Iron Age, in which it may be said we are now living.

## GEOGRAPHICAL CHANGES SINCE THE GREAT ICE AGE

RETREAT OF THE ICE AND EMERGENCE OF LAND.—It may be stated in general that the whole of the region occupied by the ice-sheet lay at a lower level than it does at the present day, which suggests the idea that the weight of the enormous accumulation of ice in high latitudes caused the depression of the surface underneath. Whether this was so or not there is no doubt that the great mass of ice must have exerted considerable attraction on the waters of the ocean, thereby raising the water level in those areas, and lowering it correspondingly in more distant regions. The retreat of the ice-sheet would bring about the reverse change, and hence it might be expected that the level of the land rose with respect to the sea, but there was a compensating influence in the large quantity of water set free by the melting of the ice.

The latter effect, being distributed over the whole ocean surface, would probably be quite small in comparison with the other, which was more localized, for it is certain that emergence of land did follow the retreat of the ice, and, moreover, it increased in amount toward the north, where the thickness of ice must have been greatest. This is shown by lines of marine beaches, the ages of which can be determined by means of their shells and other animal remains, occurring at various elevations both in northern Europe and North America. The greatest elevation does not seem to have exceeded about 500 ft. on the Atlantic coast of North America, and vanishes in the south about the forty-second degree of latitude. In Greenland the elevation also increases considerably from south to north, while in Norway shore lines with marine shells occur at altitudes of over 450 ft.

BALTIC REGION.—By far the most interesting evidence is derived from the exhaustive and careful studies carried out in the Baltic region by Scandinavian geologists (fig. 44, *a-d*). After the retreat of the main ice-sheet, that region was visited by a smaller sheet which did not penetrate far to the south, and is known as the Baltic glacier. Scandinavia was then, and until somewhat later, completely separated from the continent of Europe, for the Baltic was in free communication with the North Sea in the south and with the Arctic Ocean across Finland. As might be expected, the fauna had a decidedly northern aspect, and was characterized by the abundance of a shell called *Yoldia*, after which that sea has been called. The deposits of the YOLDIA SEA are remarkably laminated clays, the laminae varying from about  $\frac{1}{10}$  in. to  $\frac{1}{2}$  in. and are alternately of light and dark colours. An ingenious suggestion has been



made, which seems to be borne out by further study, that these laminae represent the deposits of successive seasons, the lighter layers being formed in the spring and the darker in the winter season.

A pronounced elevation then set in, which cut off communication with

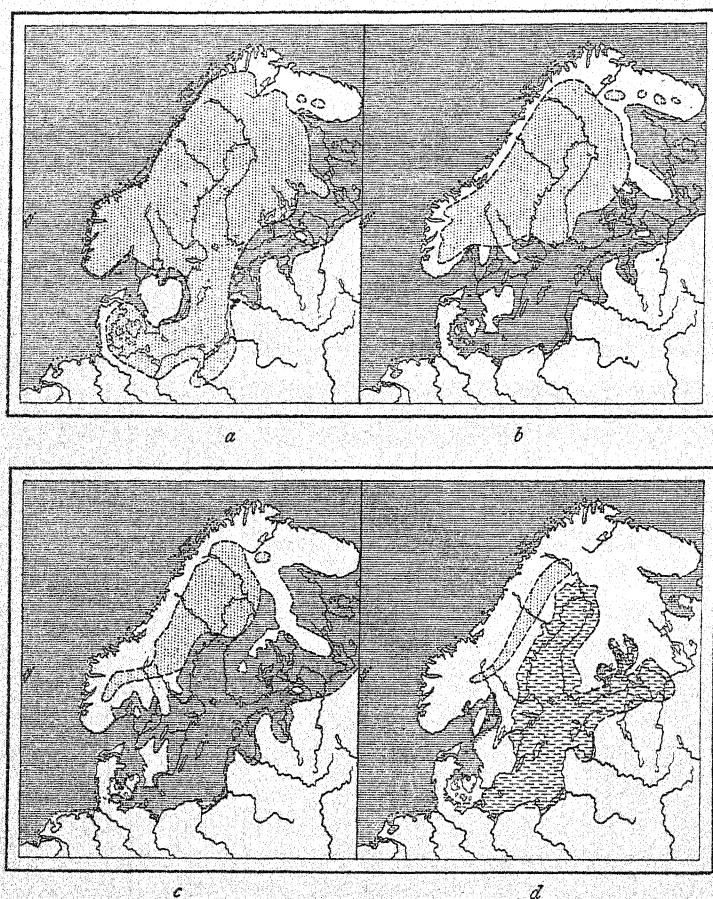


Fig. 44.—Maps showing the Changes in the Baltic Region during the Retreat of the Ice-sheet (after De Geer)

*a*, The last extension of the Scandinavian ice (Baltic glacier). *b*, The *Yoldia* Sea during the retreat of the ice. *c*, Greatest extension of the *Yoldia* Sea. *d*, The Baltic *Ancylus* Lake. The dots indicate the area covered by ice, the continuous horizontal lines represent the sea areas, and the broken horizontal lines the *Ancylus* Lake.

the ocean on the north and on the south. The fresh water which poured into the area from the rivers on all sides displaced the salt water, and gave rise to a freshwater lake known as the *ANCYLUS LAKE*, from one of the characteristic shells which lived in it. The glaciers had by this time almost vanished, but investigations have shown that the uplift took place around a line coinciding with the long axis of the ice cap. The

overflow of the lake was into the North Sea by the Sound and the Belts, which were then river channels.

Another depression let in the sea once more (the LITTORINA SEA), but this time only across the south. The entrance of the salt water at that end drove the freshwater denizens towards the north, where the marine forms followed them as far as the conditions would allow; in this way cockles and other animals reached the Gulf of Bothnia, indicating that the Baltic was at that time much more saline than the present sea. A slight elevation which followed impeded somewhat the entrance of salt water from the North Sea, and hence there resulted diminished salinity and conditions approaching those of the modern Baltic. The cockles and other typically marine forms therefore gave way to a mixed freshwater and marine life, but it is significant that in the deeper parts at the present day the water is much more salt than at the surface, suggesting that at those depths the conditions of the Littorina Sea still survive.

BRITISH AREA.—It is considered by some English geologists that at the time of the Ancylus Lake the greater parts of the North Sea and the English Channel were above the level of the sea, when the Rhine flowed out between the Shetland Isles and Scandinavia, and the Seine only reached the Atlantic outside Finisterre. In later times Britain has suffered submergence, as is indicated not only by the North Sea and the English Channel, but by the remains of forests and peat flats which are now covered by the sea, and also by the fiordlike indentations of the coasts of Devon, Cornwall, and south-west Wales, which are really drowned river valleys. Near Cardiff a submergence of about 40 ft. has taken place since Neolithic times. In Palæolithic and Neolithic times it is probable that the coasts of Britain were fringed by wide flats and marshes on which a dense vegetation grew. The various caves around the coasts have yielded the bones of hyenas and other animals which have since become extinct in these islands. They probably frequented the coastal marshes in search of food and water, and withdrew to the caves to sleep. Bone caves occur on some of the small islands in the Bristol Channel which in themselves could not have afforded the means of subsistence to the animals which lived in the caves, and therefore there must have been more or less free connection with the mainland, pointing, as does the other evidence, to a comparatively recent submergence.

The MEDITERRANEAN REGION continued to be a region of unrest, for elevations and depressions succeeded one another frequently since Pleistocene times. The immediate neighbourhood of the volcanic centres have been particularly liable to these oscillations.



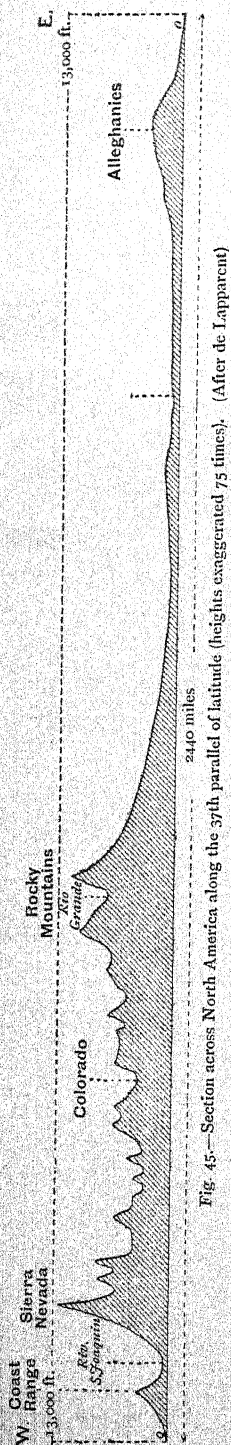


Fig. 45.—Section across North America along the 37th parallel of latitude (heights exaggerated 75 times). (After de Laparant)

**PACIFIC CORAL REEFS.**—Until recent years it was considered that the coral reefs of the central Pacific furnished indisputable proofs of the gradual subsidence of an enormous tract, but subsequent investigations have not confirmed this view; on the other hand, coral reefs were discovered in the Fiji and Solomon Isles at heights of from 50 to 100 ft. above sea-level in the former and over 800 ft. in the latter, showing that those regions at any rate must have been elevated at a comparatively recent epoch. It would perhaps not be fair to argue from these examples that the whole of the Central Pacific area was undergoing elevation. These island groups, as can be seen on a map, lie on a curved line between New Guinea and New Zealand, two regions which were theatres of mountain-building in middle Tertiary times, and are liable to be visited by severe earthquake shocks at the present day. It is not unlikely therefore that these groups represent a stage in the formation of mountain chains where the elevation has not been of sufficient amount to do more than cause the highest peaks to protrude above the level of the sea. Much greater elevations are recorded from the Pacific coast of America, for in California Pleistocene deposits are said to occur at heights of 1500 to 3000 ft. above sea level. It is possible that in those regions the Pliocene movements had not expended their energy before the succeeding period commenced.

#### EVOLUTION OF EXISTING LAND AND SEA AREAS

A rough-and-ready classification into continental and oceanic areas will serve as a convenient basis in dealing with the diverse features of the surface of the earth at the present day (see coloured plate). It is true that the history of these two areas must be to a certain extent mutually related, yet they present a number of points of difference. As an example of their interdependence, it may be mentioned that a part of the oceanic areas as ordinarily understood must be

included with the continents in any account which deals with their mode of origin; on the other hand, while the relief of the land areas is largely the result of movements of upheaval, subsequently modified and accentuated by the external agencies of denudation, the sub-oceanic features are primarily due to movements of subsidence which the subsequent process

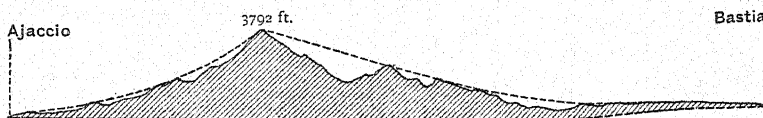


Fig. 46.—Section across Corsica (after de Lapparent)

of deposition has served rather to mollify than to accentuate. It was pointed out in a previous chapter that convex outlines are characteristic results of earth movements, but that these are destroyed and replaced by concave curves after the denuding action of running water comes into play. The ocean floor, on the other hand, is exempt from that opera-

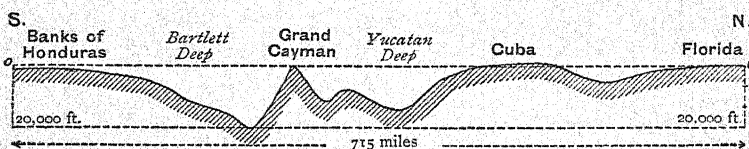


Fig. 47.—Section across the Sea of the Antilles from the Honduras Bank to Florida (after de Lapparent)

tion, and hence retains the outlines imposed upon it by the originating movement, for the accumulation of the relatively thin skin of deposits, while it tends to soften the essential features, cannot conceal them.

The distinction will be best realized by comparing fig. 45, which represents a section across the continent of North America, or fig. 46, which is a

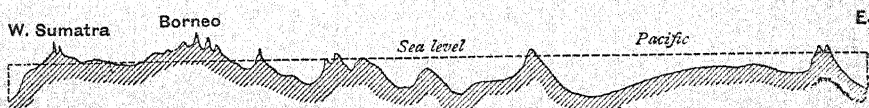


Fig. 48.—Section along the Equator from the Indian to the Pacific Ocean (after Heiderich). Vertical scale 100 times the horizontal scale

profile of the island of Corsica, with the section across the Antilles (fig. 47), or that between the Indian and Pacific oceans (fig. 48). In the two first the concave outlines are very striking, while in the two last they are exceptional. Support is lent to the idea that the peculiar features of the ocean bottom are due to subsidence, by an examination of areas of comparatively recent depression on the continents where denudation has not operated for a sufficient length of time as to leave its distinguishing mark on them.



One of the most suitable of these is the extraordinary depression in which the valley of the Jordan and the Dead Sea are situated. That sea, the surface of which is far below the level of the Mediterranean, obviously lies in a valley of depression which can be traced with the same peculiar features for nearly 200 miles. The appended section (fig. 49) brings out very clearly the general convex outline of both its bordering slopes, contrasting strongly with that from Jerusalem to Jaffa, which is due to prolonged denudation.

In dealing with the continents of the Northern Hemisphere it is convenient to proceed from north to south, for by so doing one follows the order in which the great mountain-building movements succeeded one another in course of time.

In NORTH-WEST EUROPE lies the Scandinavian peninsula, which presents to the Atlantic a marvellously intricate coast-line, behind which



Fig. 49.—Section from the Mediterranean Sea to Jerusalem and across the Dead Sea (after de Lapparent)

risers a range of steep and rugged mountains; when these are ascended, and the crest, which stands a few miles back from the coast, is reached the appearance changes to an immense plain or plateau, which slopes gently away to the Baltic in the south and Finland in the south-east. The plain is furrowed by numerous valleys, while a multitude of lakes and lakelets dot the surface as far as the eye can reach. At its lower end it subsides gradually beneath an almost continuous girdle of lakes, freshwater and marine, stretching from the Baltic across Finland to the Arctic Ocean, while a tongue is sent north as the Gulf of Bothnia, which almost severs the peninsula into two.

The peninsula is composed of pre-Cambrian rocks, among which are scattered traces of Lower Palæozoic sediments, but no younger deposits exist, except in the extreme north. It had been reduced to a peneplain before the beginning of Cambrian times, and the results of the great earth movements of the pre-Cambrian era had been obliterated. At the close of the Silurian, fresh mountains arose, the sea receded from the region, and there is no evidence that it ever after obtained a hold on that land. The prolonged denudation which it must have suffered from the Devonian period to the present has effectually removed all trace of that movement and developed a fresh peneplain.

In the Tertiary period the peneplain received a tilt in its present

direction, and hills and valleys were carved out of it in consequence; while the rugged mountainous aspect of the Atlantic frontier is due to similar agencies. The great altitude which the plateau attained on the west enabled the streams to cut down their channels rapidly and develop a complicated system of drainage. A slight submergence which occurred at a later stage had the effect of drowning the lower ends of the river valleys and allowing the sea to penetrate along them and their numerous tributaries for many miles, from which result the intricately winding inlets known as fiords which are so characteristic of this coast. The glacial episode has left its traces in the innumerable lakes and lakelets scattered over the surface. The north-west part of Britain has had a similar history to the Scandinavian peninsula, and, geologically speaking, is only an annex of it.

Turning to NORTH AMERICA, an astonishing similarity to north-west Europe reveals itself. The chain of great lakes, reaching across Canada and almost connecting the Arctic Ocean with the Atlantic, forms the border of an immense plateau of pre-Cambrian rocks stretching far to the north and north-east, on which later sediments occupy but a small area except in the extreme north. The centre is occupied by Hudson's Bay—the counterpart of the Gulf of Bothnia. The American plateau has escaped the uplift to which the extreme ruggedness of part of the European analogue is due, but the glacial episode has left its mark in numerous lakes, both large and small.

The Cambrian sediments which fringe the lake girdle of north-west Europe introduces the widely different region extending from the Urals across the Russian and north German plains to England and Ireland. Here the sea maintained its sway with minor interruptions till the close of the Carboniferous period, when a barrier of mountain chains arose, which hemmed it in almost on all sides (the Armorican chain on the south and the Ural on the east), and changed a great part of the former ocean floor to an upland region dotted over with desert areas. Again North America offers an exact counterpart. The Alleghanies and Appalachians on the east, and the early range in the Rocky Mountain region on the west, form an almost complete girdle to the enormous tract drained by the Mississippi and the Missouri—a tract of analogous geological history to the Russian plain and north central Europe.

To these must now be added another region, viz. NORTHERN ASIA from the south of Lake Baikal to the Arctic Ocean. Though offering various differences from either of the others, yet the main events in this region have been similar, for the post-Carboniferous elevation likewise



erected a mountain barrier, nearly enclosing the region, and converting it into an arid continental area.

When the crests of the Armorican mountains had been removed by never-ceasing denudation, and their cores of hard and rigid rocks laid bare, these became the foundations on which the superstructure of central Europe was raised in later times. In America too, and in Asia, the remains of the post-Carboniferous mountains play to this day an important part in the geography of those countries.

CENTRAL OCEAN—GONDWANA LAND.—While continental conditions prevailed over central Eurasia and central North America, a great ocean skirted their southern boundaries, and while during the Jurassic period the sea in the more northern regions was struggling against incessant minor uplifts to overcome the land, the great Central Ocean maintained its sway without difficulty from Panama on the west to the Pacific on the east. On the south, however, lay the great southern continent of Gondwana Land in undisputed possession of terrestrial conditions. It was only in Cretaceous times that the mastery of the sea over the northern regions became almost complete, and even Gondwana Land came under the influence of that great submergence.

LAST GREAT UPHEAVAL.—This triumph of the ocean was, however, short-lived, for immediately there began the greatest upheaval that has affected the earth's surface since the beginning of sedimentation. North America and Eurasia were raised above the sea, while the great Central Sea lost one after another its possessions, and mighty mountain chains arose around its margins and within its boundaries. The extent of that movement may be gauged from the fact that deposits which were laid down on the floor of the Central Sea now occur on the plateau of Tibet at a height of over 20,000 ft. It seems to have affected especially those areas where marine conditions prevailed during the Mesozoic period, for another region which shared this characteristic with the Central Sea was influenced by great earth movements for the first time in its history. This was the Pacific border, which is now occupied by an almost continuous girdle of mountain chains, presenting on a map a remarkable festoon-like arrangement. Were Antarctica better known it would probably be found that the chain extended across it, thus completing the girdle now terminating at South America on the one hand and at New Zealand on the other.

The effects of the movement have not yet died away, for along the whole extent of the Pacific border volcanic activity is rife, while severe earthquake shocks are of frequent occurrence.

Since that important episode only minor changes have affected the earth's surface, and as these have been outlined on previous pages it is unnecessary to repeat them.

THE SOUTHERN LAND MASSES.—The continents of South Africa and Australia and the Indian Peninsula have much in common at the present day. They all form elevated plateaulike regions, which, for the most part, descend abruptly towards the coast; the interiors of all three are under desert conditions, while true mountain chains are almost absent, the exceptions being of earlier date than the Carboniferous. These resemblances are but reflections of their closely allied geological history. Palæozoic sediments enter but slightly into their constitution, and therefore there must have been enormous land areas in the Southern Hemisphere during that era; again, while marine sediments were forming over wide regions in the Northern Hemisphere during the Secondary and early Tertiary periods, these continents, which were probably connected together, were undergoing glaciation, followed by a desert regime. Volcanic activity on an extensive scale prevailed in South Africa and India, and probably also in South America; while at more than one stage during the period great subsidences occurred, which have left a profound impression on their physical geography, as evidenced by the abrupt descent from the plateau to the coast-line and the extraordinary rift valley of Africa—a veritable trough of subsidence. The chief characteristic common to these areas is their freedom from mountain-building movements.

THE HISTORY OF THE MODERN OCEANS.—One striking fact in regard to the great oceanic areas of to-day is that they are of very different ages and have arisen in radically different ways. There is much reason to assign to the PACIFIC an origin which dates from an early stage in the earth's history. It was, indeed, probably represented by the original hollows, in which water began to collect on the surface, though it has gained enormously in extent and in depth as the result of subsequent changes. No great movement affected its margins until middle Tertiary times, but its capacity had steadily increased by gradual subsidence of its floor. Even the mountain-building episode probably increased its depth, the rise of land along its boundary being attended by an opposite change just within, for it is a striking fact that those places where the bottom descends to the enormous depth of over 5 miles nearly all occur close in front of the mountain girdle, while the central portions stand on an average at considerably higher levels. Active volcanoes rising out of profound depths suggest that movements of the floor are still in progress.



The ATLANTIC and INDIAN OCEANS have a different history. Until the end of the Secondary period, if not later, they formed for the most part land areas, except along the centre of the Atlantic, where the Central Sea divided it into a northern and a southern portion. The present Atlantic ocean has arisen by a widening of the margins of that sea, whereby Atlantis on the north and Gondwana Land on the south sank to the depths by faulting. The wedge of Greenland still survives as a sector of the ancient northern land.

The ARCTIC OCEAN, like the Pacific, is probably of early origin, but unlike that ocean it has been immune from violent earth movements, at any rate since the pre-Cambrian period.

CONTINENTAL SHELF.—Around the borders of the north Atlantic the sea floor shelves gradually to about 100 fathoms, after which it plunges to great depths. The continents therefore stand on a submerged platform as on a pedestal, and if an uplift of about 100 fathoms were to occur, the outline of the north Atlantic coast, now so intricate, would become much simplified, and many scattered islands would be united to the mainland. There would then be no shelving shore, but one that plunged suddenly to a great depth. The CONTINENTAL SHELF is narrow around the southern continents, and is as good as absent around the Pacific. That it should be regarded as part of the bordering continent, and not of the ocean, is shown by the fact that the land features are continued across it, for opposite the mouths of most of the large rivers occurs a deep trench, which extends to the outer limit of the shelf; the sides and bottom of the trench have the characteristic form of those of river valleys, but modified somewhat by a covering of sediment, and it is almost certain that they are in reality submerged valleys. On this view the shelf has been formed by the wear of the sea on the margin of a land which was slowly being submerged. The outer limit of the shelf is therefore the real limit of the continental area; the part beyond belongs to the ocean, and has a different geological history.

A comparison of the Atlantic and Pacific basins brings out the interesting fact that the area of land draining into them bears no proportion to that of the oceans, for although the area of the Pacific is more than double that of the Atlantic, yet the latter receives more than half the drainage of the whole earth's surface; the Pacific and Indian Oceans combined only receive about a quarter, which is only slightly greater than that which never reaches any ocean. This is largely due to the elevation of the chain of mountains in Tertiary times so close to the Pacific border. The large proportion of the drainage which never reaches

any ocean is striking. In those regions desert conditions prevail, and part of the water is absorbed by the desert or evaporated, while a part flows into inland seas like the Caspian, which have no outlet, and where therefore the water is brackish. The prevalence of desert conditions, the extent of territory without communication with the ocean, and the considerable altitude of the continents on an average, suggests that we are still living in a continental period following the mid-Tertiary elevation, and that the cycle of denudation has only partly run its course.

#### THE BEARING OF GEOLOGICAL AND GEOGRAPHICAL CONDITIONS UPON THE DEVELOPMENT OF THE HUMAN RACE

PLACE OF ORIGIN.—It has already been mentioned that great uncertainty prevails as to the precise period when the first human beings appeared. No less uncertainty exists in regard to the part of the earth's surface where they originated, though the general opinion seems to be that it was somewhere in southern Asia, whence migrations to east, west, north, and south peopled the rest of the habitable globe. It is not clear, however, that future discoveries may not prove the claims of Africa to be at least as strong as those of southern Asia; they may also tend to show that human characteristics developed simultaneously, or nearly so, at more than one centre. Our general ignorance of so much of the interior of Africa, however, forbids more than a bare suggestion.

LINES OF MIGRATION.—Adopting the generally received view that the human race originated somewhere in the warm and relatively dry tracts of southern Asia, it is probable that four great movements of migration started from that centre. These were controlled to an important degree by the geographical conditions of that region, hemmed in, as it was, on one side by the vast arid plateau of central Asia, and on the other by the ocean.

The first great movement was towards the east and north-east, along the Pacific border, and thence down along the whole length of the American continent. A second movement to the south-east peopled Australia and neighbouring islands, while a third to the south-west gave rise to the negro races of Africa, and a fourth important movement towards the north-west is responsible for the various races of Europe and western Asia. The lines of migration followed of necessity the more fertile tracts along the river valleys or near the coasts, and for this reason the valleys of the Euphrates and Tigris offered exceptional facilities. It has been pointed out by the American geologists Chamberlin



and Salisbury, from whom some of the above suggestions are adopted, that the centres of early civilization were all regions of high barometric pressure, and of rather arid climate, which they consider must have been specially favourable to mental and physical activity. It is suggested also that early man would find it easier to cultivate and water certain selected plants in a relatively arid region than to cope with the wealth of vegetation in a moist region, and to select those plants which would be of use to him. Whether this is so or not, there is no doubt that the pursuit of agriculture must have contributed not a little to a fixed abode, and consequently to the growth of a social organization.

MEDITERRANEAN REGIONS.—For some reason or combination of reasons the Mediterranean region seems to have offered special facilities for the development of the activities of man, for the early seats of Western civilization have all centred around it. Egypt, Greece, and Rome became in turn the seats of intellectual activity, and it has been remarked that successive civilizations followed one another northward towards a more rigorous and stimulating climate, and that the same tendency is shown at the present day.

In one respect the favourable influence of the Mediterranean can be easily understood. A large seaboard to a comparatively tideless sea, free from violent storms for a great part of the year, though destructive enough when they occurred, taught man to cope with and master the difficulties of navigation, and as he became more proficient he was able to venture forth to the open ocean, thus disseminating trade to distant regions, and spreading the rudiments of civilization to less favoured countries.

SCANDINAVIAN PENINSULA.—At a later period another region shared with the Mediterranean the honour of having incited the human race to go "down to the sea in ships". The Scandinavian peninsula, with its innumerable fiords, sheltered from the violence of the Atlantic waves, allowed ill-equipped primitive man to carry on nautical experiments with a comparative degree of safety; while the Baltic Sea, with its many inlets, may be compared with the Mediterranean, and may be assigned a similar rôle. There is this difference, that the rigorous climate which the northern races had to contend with developed in them traits of hardihood, endurance, and doggedness which have survived to their descendants, and have contributed not a little to their success; while the southern regions, with their sunny climate and their bright surroundings, incited the artistic temperament and developed corresponding traits in those peoples.

INFLUENCE OF PHYSICAL FEATURES.—To the early races high

mountain barriers offered serious impediments to free communication, and consequently civilization in such regions lagged behind that of the more favoured peoples who inhabited fertile, low-lying, well-watered tracts. As the competition increased, less favourable areas came to be utilized of necessity, and fresh means had to be discovered to make them habitable. One of the most important conditions which determined a settlement was a suitable supply of water, and it has been noticed that in the east of England, at the present day, the sites of villages tend to follow the out-crop of certain rocks, which throw out water in the form of springs. When sterile tracts had to be resorted to, water was often obtained by sinking wells, an operation which has rendered many regions habitable which were formerly unsuitable. This method is being employed on a large scale to-day, and in Africa enormous tracts along the borders of the Sahara have been reclaimed to cultivation by means of water obtained in this way.

IMPORTANCE OF MINERAL DEPOSITS.—It will be seen, therefore, that man is dependent upon modern geological and geographical conditions to a greater extent than he is accustomed to believe, but this is trivial as compared with his indebtedness to conditions which prevailed long ages ago, and have since passed away. For even his SALT is a legacy of those oft-repeated continental conditions which attended the formation of great mountain chains in the past; the remains of those chains are to-day so insignificant that only by patient research can the geologist affirm with confidence that they ever existed. The METALS he uses are many of them found in the oldest rocks which appear at the surface of the earth, while the GOLD with which he buys them is derived almost exclusively from such rocks.

COAL.—Lastly, the peculiar conditions which enabled a luxuriant growth of vegetation to flourish in the far-off Carboniferous period have placed at his command to-day an unrivalled source of energy, which he squanders with lavish prodigality, even in the face of the authoritative statement of a Royal Commission that, at the present rate of consumption, one of the most important coal supplies, that of the British Isles, will be exhausted within the next four hundred years.

As the other known coal supplies must also give out within a comparatively short period of time, it is evident that in the future man must turn to other sources of energy. It is, of course, possible that with the progress of geological knowledge other coalfields may yet be discovered, but even taking into account all the fields known at present, and others yet unfound, it is certain that, as a source of energy, the coal supplies of



the world must be used up within a period of time, large though it may be in comparison with the average life of a human being, yet utterly insignificant beside the period during which the earth has existed in the past, and is likely to exist in the future. Attention is already being turned to auxiliary sources, some of which are direct consequences of geological causes. The waterfalls, which are characteristic of late changes in the earth's crust, may attain an importance hitherto unsuspected, and they have the advantage of a probable term of existence and usefulness far exceeding that of current supplies. It has been suggested also to use the direct rays of the sun, wind-power, and the restless activity of the tides, each of which would undoubtedly be of considerable service, but should these prove insufficient, means may be discovered which are as yet undreamt of. But of the destinies of the human race when that time shall come no one has been bold enough to prophesy.

# LIST OF GEOLOGICAL WORKS RECOMMENDED FOR FURTHER STUDY

Name.	Author.	Publishers.
THE SCENERY OF ENGLAND	Lord Avebury	Macmillan & Co.
THE SCENERY OF SWITZER- LAND ... }	"	"
GEOLOGY (3 vols.) ... }	T. C. Chamberlin and R. D. Salisbury	Henry Holt & Co., New York.
CLIMATE AND COSMOGONY ...	James Croll	Edward Stanford.
MANUAL OF GEOLOGY ...	J. D. Dana	{ Kegan Paul, Trench, Trübner & Co.
PHYSICAL GEOGRAPHY ...	Prof. W. M. Davis	Ginn & Co.
THE ANCIENT VOLCANOES OF BRITAIN (2 vols.) }	Sir A. Geikie	Macmillan & Co.
THE SCENERY OF SCOTLAND	"	"
TEXTBOOK OF GEOLOGY (2 vols.) ... }	"	"
THE GREAT ICE AGE	Prof. J. Geikie	Appleton & Co.
STRUCTURAL AND FIELD GEOLOGY ... }	"	Oliver & Boyd.
LEHRBUCH DER GEOLOGIS- CHEN FORMATIONSKUNDE (2 vols.) ... }	E. Kayser	Ferdinand Enke, Stutt- gart.
TEXTBOOK OF COMPARATIVE GEOLOGY (Trans. from Kayser's LEHRBUCH) }	P. Lake	Swan Sonnenschein & Co.
TRAITÉ DE GÉOLOGIE ...	A. de Lapparent	Masson et Cie, Paris.
LEÇONS DE GÉOGRAPHIE PHYSIQUE ... }	"	"
PRINCIPLES OF GEOLOGY (2 vols.) ... }	Sir C. Lyell	John Murray.
THE PRINCIPLES OF STRATI- GRAPHICAL GEOLOGY }	J. E. Marr	Cambridge University Press.
THE SCIENTIFIC STUDY OF SCENERY ... }	"	Methuen & Co.
DIE MORPHOLOGIE DER ERDOBERFLÄCHE (2 vols.) }	A. Penck	J. Engelhorn, Stuttgart.
RIVER DEVELOPMENT ...	I. C. Russell	John Murray.
PHYSIOGRAPHY ...	R. D. Salisbury	John Murray.
DAS ANTLITZ DER ERDE (3 vols.) ... }	Prof. Edward Suess	F. Tempsky, Vienna.
THE FACE OF THE EARTH (2 vols. published) }	Trans. of preceding by Prof. W. J. Sollas and Hertha B. C. Sollas	Clarendon Press, Oxford.





# CHEMISTRY

BY

J. P. MILLINGTON, M.A., B.Sc.



# CHEMISTRY

## CHAPTER I

### HISTORY OF CHEMISTRY

NATURE OF THE SUBJECT.—From the earliest times civilized man has been concerned with the problem of the nature of matter. So soon as he raised himself above the level when the only needs to be satisfied were those of the body, he turned his attention to all that lay around him, to all that he could see and touch. In other words, he became interested in MATTER. This interest has widened and deepened during man's intellectual development, and the result is that branch of knowledge known to-day as Natural Philosophy. One division of this vast subject is CHEMISTRY, which is more particularly concerned with certain changes undergone by matter. Changes in matter fall under two main headings, namely, physical and chemical, but the distinction between them is not by any means a sharp one. Every CHEMICAL CHANGE or reaction is accompanied by some physical change, such as the evolution of heat or light, or the appearance of electrical phenomena, so that the study of these two branches of Natural Philosophy is generally and to the best advantage undertaken at the same time. In the following account we shall deal mainly with those manifestations of the properties of matter which are usually treated under the heading of Chemistry.

EGYPT, INDIA, GREECE.—The earliest indications we have of man's thoughts on the subject of matter are to be found in the ancient writings of Egypt and India, but it is not until the time of the early Greek schools that we find any clear account of the directions in which thought was tending. There were two views as to the structure of matter. One was that matter was continuous and capable of an infinite amount of division, while the other view presented it as being made up of a vast number of discrete particles, infinitesimal in size and unchanging in nature. It is this latter



view which has been most helpful in scientific thought, and in recent times it has been advanced to the dignity of a hypothesis.

Thales looked upon water as the basis of all things. From water the earth seemed to spring, and water was taken up by the air and disappeared, so water must be the foundation of life and matter. Later, Anaximenes, and after him Diogenes, taught that air was the parent substance and could assume qualities by means of which it was converted into one or other of the four "elements"—fire, earth, air, or water. Earth and water were formed by precipitation or condensation, but it is impossible to see in what respects the "element" air differs from the parent substance.

Anaxagoras regarded matter as being made up of the same four "elements", but held that these were formed of an infinite number of minute particles, and according as one kind of particle was in excess, there resulted a certain kind of matter. This idea was also held by Zeno and Empedocles, who emphasized the unchanging nature of the particles.

The greatest advance, however, was made by the philosophers Leucippus and Democritus, who first suggested that the various properties of matter depended upon the arrangements of the particles or atoms. They also introduced the conception that the atoms possessed the power of motion. These views were elaborated by the Epicurean school, and were later adopted by Lucretius as the basis of the scheme of the universe which he embodied in his principal work, *De Rerum Natura*. In this poem he speaks of matter as being, not "mingled and massed into indissoluble union", but as made up of "prime material atoms" possessing an inherent elasticity which "drives them about space vagrantly onward . . .".

THE ALCHEMISTS.—After these philosophical speculations of the early Greeks there is nothing worthy of mention until we reach the times when Chemistry, in the form of alchemy, began to be studied as a separate science. The clear conception of Lucretius became overlaid with mysticism, and the original idea of the "elements", unchangeable in nature, was lost sight of. Albertus Magnus regarded the birth of one element as being due to the death of another, a view which to-day is held by some chemists. He thought that there was, as the basis of all matter, some prime substance which, when combined in different ways, became matter as revealed to the senses. To this primordial substance the name *yle* was given by Roger Bacon, who flourished about the same time as Albertus Magnus. It was this hypothesis that guided the thoughts of the alchemists to the possibility of transforming one substance, or, as we now say, element, into another.



The pursuit of science, if alchemy can be dignified with the name of a science, was undertaken, not for the sake of truth, but for the sake of the power which gold can buy. The dream of every alchemist's life was the discovery of the philosopher's stone, which by its magic touch could convert base metals into gold. No one sought to convert gold into lead. Geber, rather more rational than the rest of his fellows, believed in the transmutation of metals by nature, but denied to man the power of effecting a like change.

Gradually the search for the philosopher's stone was abandoned, and every alchemist dreamed of finding an elixir which should prove a sovereign cure for all ills, and greatly prolong life. Although these dreams never came true, science was enriched, for many new substances were discovered, some of which are still used in medicine, as, for example, antimony, corrosive sublimate, and perchloride of iron.

ROBERT BOYLE.—The transition from alchemy to scientific chemistry occurred when Robert Boyle published his epoch-making work, *The Sceptical Chymist*. He abandons the old ideas of the elements earth, air, fire, and water, and upholds the modern view, of simple bodies which so far have resisted all attempts to resolve them into still simpler ones.

From the time of Boyle onwards this conception has held sway, and, from the chemist's point of view, matter is still regarded in much the same light as it was by Boyle. Newton held similar views, for he writes: "It seems probable to me that God in the beginning formed matter in solid, massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced to the end for which He formed them".

PHLOGISTIC THEORY.—Once again comparatively clear and definite views were obscured and made indefinite by the introduction of further hypotheses. Becher and Stahl thought that in addition to the fundamental constituents of matter there was present in all combustible bodies a *terra pinguis*. This *terra pinguis*, or PHLOGISTON as it was called by Stahl, escaped during combustion, sometimes with such intensity as to produce flame. When a metal was burned in air there was left a powder which was called a *calx*, and a metal was thus looked upon as a compound of a calx and phlogiston. After the discovery of oxygen by Priestley, and the work of Cavendish on the composition of water, the phlogistic theory could no longer be maintained, and the true explanation of the phenomena of combustion was furnished by Lavoisier.

Towards the end of the eighteenth century, however, a more definite view emerged from the mass of hypotheses which had grown round the

earlier ideas. The atom once again came into prominence, and the old theory of matter, as being composed of an infinite number of discrete particles, was revived.

**DALTON'S ATOMIC HYPOTHESIS.**—The enunciation of the atomic hypothesis by John Dalton marks the beginning of a new epoch. For the first time speculations as to the atomic nature of matter were something more than merely qualitative. By experiment Dalton showed that there were some definite rules underlying the combination of atoms, and these rules are to-day known as the **LAWS OF CHEMICAL COMBINATION**.

Attempts have not been wanting to prove that the credit of this view must not be given to Dalton, but the balance of evidence seems to show that he first clearly saw how the constancy of composition of chemical compounds could be explained by assuming that the elements combined together in fixed proportions by weight. It was universally believed at one time that Dalton enunciated his laws as the result of his experiments, but later research tends to prove, wellnigh conclusively, that he first conceived the idea of combination occurring between atoms and then set out to find facts in support of his theory.

In his work entitled *A New System of Chemical Philosophy* he states quite clearly his views on the structure of matter. He writes as follows: "All bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, or atoms, of matter bound together by a force of attraction, which is more or less powerful according to circumstances, and which, as it endeavours to prevent their separation, is very properly called, in that view, attraction of cohesion, . . . or, more simply, affinity". Not content with a mere qualitative expression of the theory, Dalton set about determining the relative weights of the atoms, and the numbers he obtained are the earliest **ATOMIC WEIGHTS**.

**GAY-LUSSAC, WOLLASTON, AND AVOGADRO.**—This conception of the structure of matter received great support when Gay-Lussac discovered the law still known by his name. This law states that when gases take part in a chemical change, the reacting volumes bear a simple relation to each other and to the volume of the resulting product. The further development of the atomic hypothesis was assisted by the investigations of Wollaston on equivalents, and by the enunciation of Avogadro's rule. This rule says that under similar conditions of temperature and pressure equal volumes of all gases contain an equal number of molecules.

**ATOMS AND MOLECULES.**—A distinction was then drawn between **ATOMS** and **MOLECULES**. The former are defined as the smallest particles of matter that are capable of taking part in a chemical reaction, while the



latter are the smallest particles that can exist in a free state. In some cases the atom is identical with the molecule, or, in other words, the molecule consists of but one atom; in other cases the molecule is made up of two or more atoms.

**KINETIC THEORY OF GASES.**—In 1857, Clausius, reviving an old idea of Bernoulli, proposed what is now known as the kinetic theory of gases. This theory, further elaborated by Clerk-Maxwell and Boltzmann, regards the particles of which matter is composed as being in a constant state of motion. The molecules move about with great velocity and constantly come into contact with one another.

**MODERN VIEW OF NATURE OF MATTER.**—The usually accepted view of the nature of matter may be briefly summed up as follows: Matter is made up of a certain number of simple bodies known as **ELEMENTS**. By no known means can an element be resolved into any simpler substance. Matter as revealed to the senses, although apparently continuous, is not really so, but is made up of an infinite number of exceedingly small particles or **ATOMS**. When an element is set free from combination it can only exist in the form of a **MOLECULE**. This may consist of one or more atoms, and is capable of free and independent existence. Such particles of matter, however, are not in a state of rest, but in one of constant motion, moving about with great velocity and impinging upon other particles. In the solid state of aggregation the freedom of motion of the particles is much less than in the gaseous state, while in the liquid state it is greater than in the solid, but less than in the gaseous state.

At the present time about eighty elements are known, a list of which and their relative or atomic weights is given on p. 36.

**PROUT'S LAW.**—It will be noticed that, although some of these atomic weights are simple multiples of that of hydrogen, yet there are some which are not. Early in the nineteenth century Prout suggested that all atomic weights were simple multiples of that of hydrogen. In spite of the fact that the researches of Berzelius showed that no such simple relation held, many workers have attempted to establish the truth of this hypothesis. Prout thought that all elements could be regarded as formed from hydrogen by a process of condensation, and this view was upheld by Sir Norman Lockyer as a result of his spectroscopic investigations.

**LOCKYER.**—On examination of the spectra of the hottest stars, Lockyer found that the principal lines present were those of hydrogen, but that in the sun and other stars which do not belong to the hottest class other elements could be recognized. This led to the view that at extremely high temperatures all elements were resolved into hydrogen. More recent

## LIST OF THE ELEMENTS

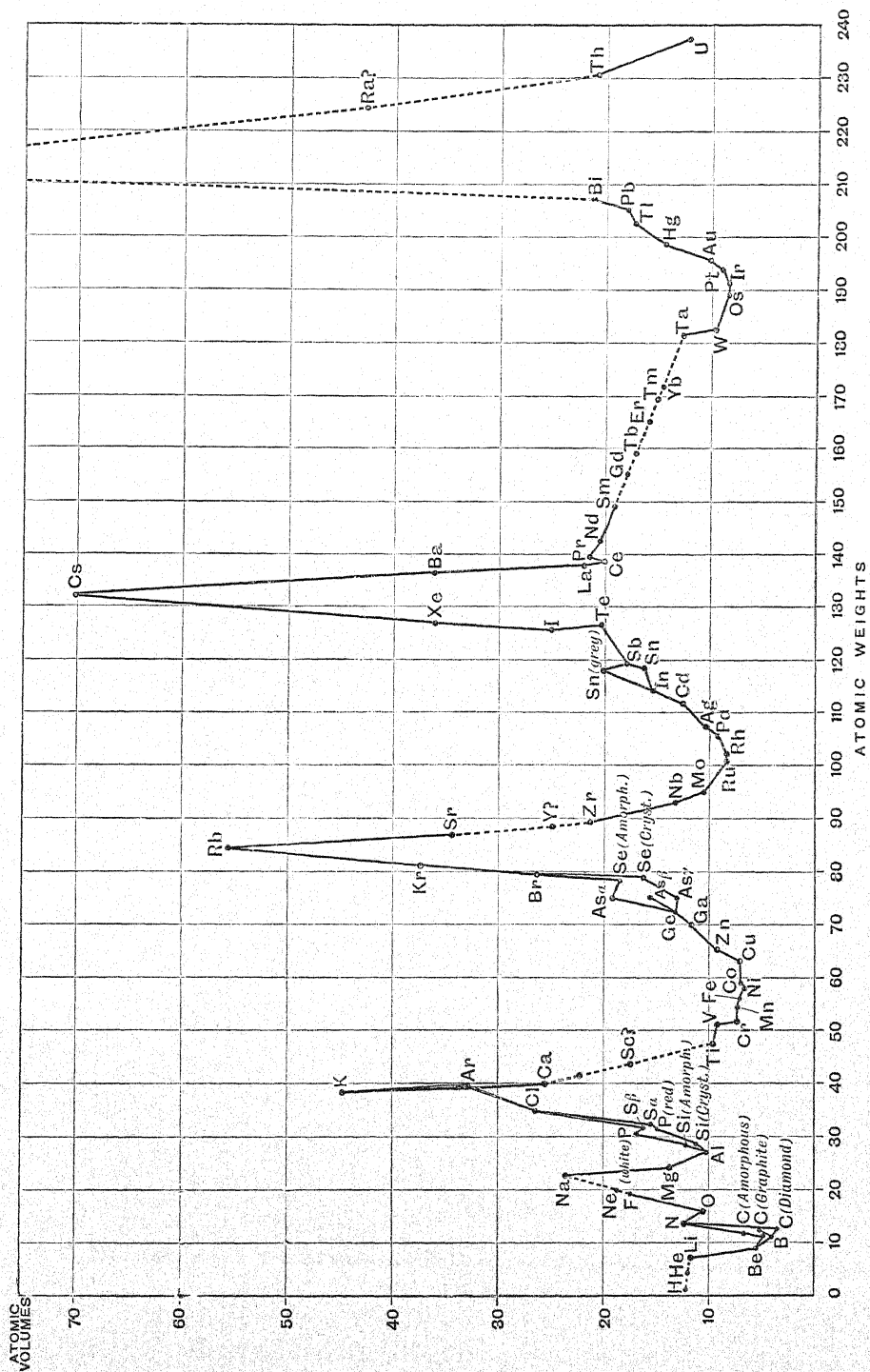
WITH THEIR SYMBOLS, ATOMIC WEIGHTS, AND ATOMIC VOLUMES

Element.	Sym- bol.	Atomic weight.	Atomic volume.	Element.	Sym- bol.	Atomic weight.	Atomic volume.
Hydrogen...	H	1	12.1 (absolute 0°)	Krypton.....	Kr	81.2	37.7
Helium.....	He	4	?	Rubidium.....	Rb	84.9	55.8
Lithium.....	Li	6.98	11.8	Strontium.....	Sr	86.94	34.8
Beryllium...	Be	9.03	5.5	Yttrium.....	Y	88.3	?
Boron.....	B	10.9	{ 4.1 (crystalline)	Zirconium.....	Zr	89.9	21.1
			{ 4.4 (amorphous)	Niobium.....	Nb	93.3	13.2
			{ 3.4 (diamond)	Molybdenum...	Mo	95.3	10.6
Carbon.....	C	11.91	{ 5.1 (graphite)	Ruthenium.....	Ru	100.9	8.4
			{ 6.8 (amorphous)	Rhodium.....	Rh	102.2	8.5
Nitrogen.....	N	13.93	12.74 (absolute 0°)	Palladium.....	Pd	105.7	9.3
Oxygen.....	O	15.88	10.6 (absolute 0°)	Silver.....	Ag	107.11	10.2
Fluorine.....	F	18.9	17.1 (liquid)	Cadmium.....	Cd	111.6	12.8
Neon.....	Ne	19.9	?	Indium.....	In	114.1	15.4
Sodium.....	Na	22.88	23.6	Tin.....	Sn	118.1	16.2, 20.2 (grey)
Magnesium...	Mg	24.18	13.8	Antimony.....	Sb	119.3	18.0
Aluminium...	Al	26.9	10.1	Tellurium.....	Te	126.6	20.4
			{ 11.3 (crystalline)	Iodine.....	I	126.01	25.5
Silicon.....	Si	28.2	{ 12.0 (amorphous)	Xenon.....	Xe	127	36.1
			{ 14.7 (red)	Cæsium.....	Cs	131.9	69.9
Phosphorus...	P	30.77	{ 16.8 (white)	Barium.....	Ba	136.4	36.4
			{ 15.4 (α)	Lanthanum.....	La	137.9	22.4
Sulphur.....	S	31.82	{ 16.2 (β)	Cerium.....	Ce	139.2	19.8
Chlorine.....	Cl	35.18	26.5	Praseodymium...	Pr	139.4	21.5
Potassium....	K	38.85	44.4	Neodymium....	Nd	142.5	20.5
Argon.....	Ar	39.6	33.0	Samarium.....	Sm	149.2	19.3
Calcium.....	Ca	39.7	25.6	Gadolinium....	Gd	154.8	?
Scandium....	Sc	43.8	17.5 (?)	Terbium.....	Tb	158.8	?
Titanium.....	Ti	47.7	9.8	Erbium.....	Er	164.7	?
Vanadium..	V	50.8	9.2	Thulium.....	Tm	169.7	?
Chromium..	Cr	51.7	7.5	Ytterbium.....	Yb	171.7	?
Manganese..	Mn	54.6	7.3	Tantalum.....	Ta	181.6	12.9
Iron.....	Fe	55.5	7.1	Tungsten.....	W	182.6	9.8
Nickel.....	Ni	58.3	6.6	Osmium.....	Os	189.6	8.5
Cobalt.....	Co	58.55	6.9	Iridium.....	Ir	191.5	8.5
Copper.....	Cu	63.1	7.1	Platinum.....	Pt	193.3	9.0
Zinc.....	Zn	64.9	9.1	Gold.....	Au	195.7	10.2
Gallium....	Ga	69.5	11.7	Mercury.....	Hg	198.5	14.6
Germanium..	Ge	72	13.1	Thallium.....	Tl	202.6	17.2
			{ 13.0 (γ)	Lead.....	Pb	205.35	18.1
Arsenic.....	As	74.4	{ 15.8 (β)	Bismuth.....	Bi	206.9	21.2
			{ 19.2 (α)	Radium.....	Ra	223.3	?
Selenium....	Se	78.6	16.4 to 18.5	Thorium.....	Th	230.8	21.0
Bromine.....	Br	79.36	26.7	Uranium.....	U	236.7	12.7

work has shown, however, that even in the hottest stars another element, namely, HELIUM, can be detected. This theory has in consequence been abandoned, but within the last few years the interesting question of the possibility of transforming one element into another has received fresh attention.

RADIUM.—In 1903 Ramsay and Soddy showed that the recently discovered element RADIUM changes spontaneously into helium, and upon





CURVE OF ATOMIC VOLUMES





this fact new speculations have been based as to the possibility of the elements as known to us being only stages in the formation of others, or even of being aggregates of some more simple state of matter.

NEWLANDS'S LAW OF OCTAVES.—As long ago as 1863 Newlands pointed out that certain relations existed between the atomic weights of the elements and their properties. He showed that if they are arranged in order of increasing atomic weight, the properties tend to recur in periods of seven. This observation he designated by the name of the "Law of Octaves".

PERIODIC SYSTEM OF LOTHAR MEYER AND MENDELÉEFF.—In 1864 this idea was expanded by Lothar Meyer and by Mendeléeff, who independently and almost simultaneously published tables of the elements arranged in the order of their atomic weights. It was Mendeléeff who made the most elaborate investigations on this point, and at the present time the system of classification of the elements known as the PERIODIC SYSTEM is always associated with his name. He stated that the properties of the elements were periodic functions of the atomic weight, and in his later work justified this conclusion in a remarkable manner. Since the publication of the original table many new elements have been discovered, but, broadly speaking, the law is as true to-day as when it was first enunciated. In the table on p. 38 the known elements are arranged according to this system, and it will be noticed that those having similar properties fall into well-defined groups. The groups are further divided into sub-groups, in order to bring out more clearly the relations which hold between these elements.

Elements so closely allied chemically as lithium, sodium, potassium, rubidium, and caesium fall into one group. So do the metals of the alkaline earths, the members of the nitrogen group, and the halogens.

In addition to the periodicity of chemical properties a similar state of things is noticed when the physical properties are compared.

ATOMIC VOLUMES.—In 1870 Lothar Meyer prepared a curve illustrating the periodicity of the atomic volumes. (The atomic volume is the atomic weight divided by the density of the element in the solid form.) The accompanying curve brings out quite clearly the fact that in this respect the property of the element is a periodic function of the atomic weight.

On examination of this curve it will be seen that elements having similar properties occur in corresponding positions. Thus, for example, the alkali metals occur at the maxima (highest points) of the different portions of the curve, while the three groups of elements—iron, nickel, and

TABLE SHOWING PERIODIC ARRANGEMENT OF THE ELEMENTS WITH APPROXIMATE ATOMIC WEIGHTS

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Helium 4	Lithium 7	Boron 11	Carbon 12	Nitrogen 14	Oxygen 16	Fluorine 19	...
Neon 20	Sodium 23	Aluminium 27	Silicon 28.5	Phosphorus 31	Sulphur 32	Chlorine 35.5	...
Argon 40	Potassium 39	Scandium 44	Titanium 48	Vanadium 51	Chromium 52	Manganese 55	Iron 56  Nickel 58.7  Cobalt 59
...	Copper 63.5	Gallium 70	Germanium 72	Arsenic 75	Selenium 79	Bromine 80	...
Krypton 82	Rubidium 85.5	Yttrium 89	Zirconium 90.5	Niobium 94	Molybdenum 96	...	Ruthenium 102  Rhodium 103  Palladium 106
...	Silver 108	Indium 114	Tin 118.5	Antimony 120	Tellurium 127	Iodine 126.9	...
Xenon 128	Cesium 133	Lanthanum 138	...	...	...	...	...
...	...	...	...	...	...	...	...
...	Gold 197	Ytterbium 173	Lead 207	Tantalum 183	Tungsten 184	...	Osmium 191  Iridium 193  Platinum 195
...	...	Thallium 204	Thorium 232	Bismuth 208	Uranium 240	...	...



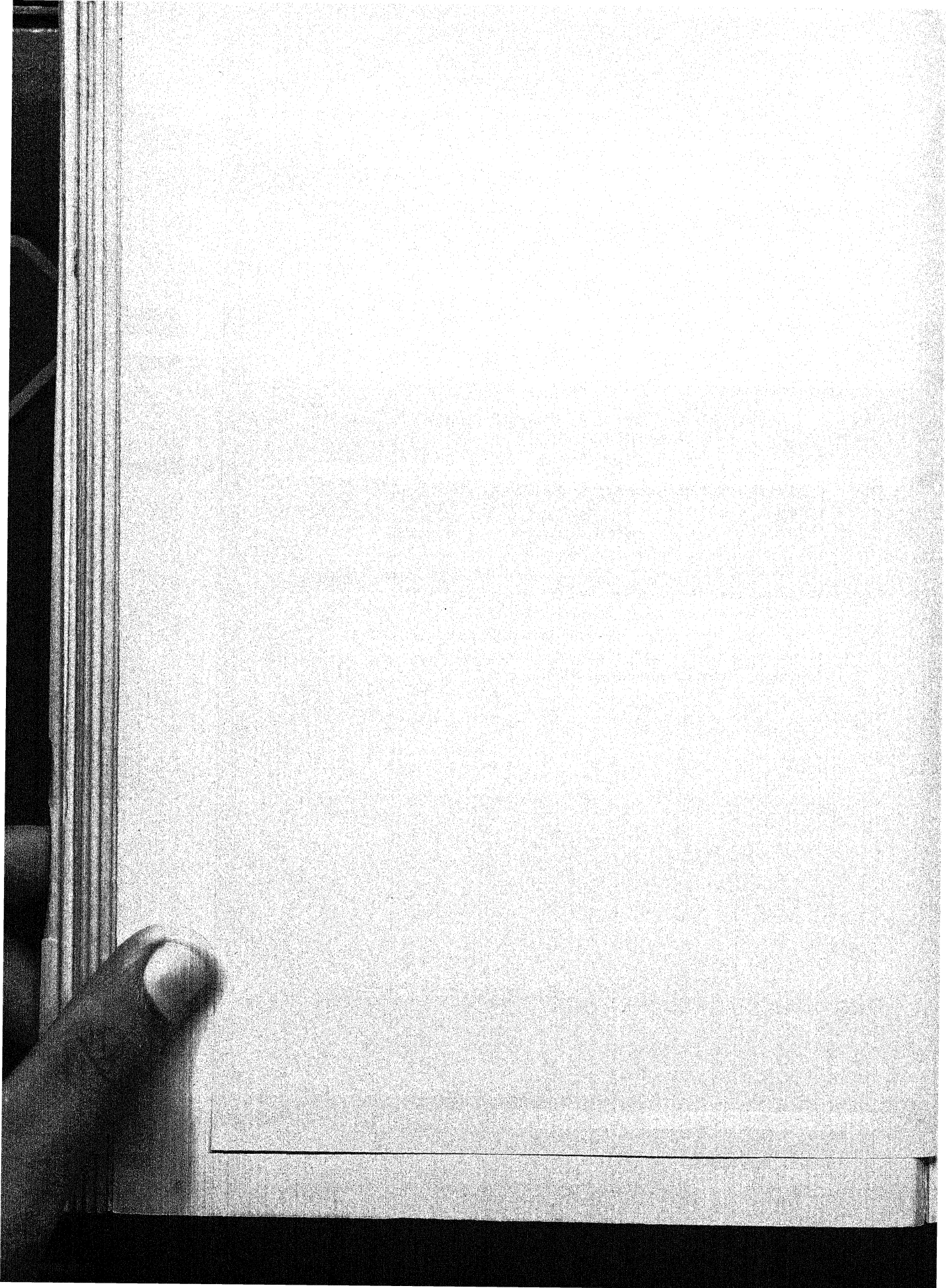
### SPECTRA OF THE ATMOSPHERIC GASES AND OF HYDROGEN

The spectrum of Argon varies according to the pressure in the Plücker tube, and also according to the intensity of the electric current.

With a strong current and a low pressure (below 1 mm.) the spectrum is rich in blue lines,  $F_2$ ; when the pressure is 3 mm. the red lines,  $F_1$ , are well marked; and when still higher (from 100 to 200 mm.) the green spectrum,  $F_3$ , is obtained.

The two faint red lines are common to all the spectra.

The spectrum of Helium is chiefly remarkable on account of the prominent yellow line which was noticed in the Solar spectrum long before terrestrial Helium was discovered.







H



G



F<sub>3</sub>



F<sub>2</sub>



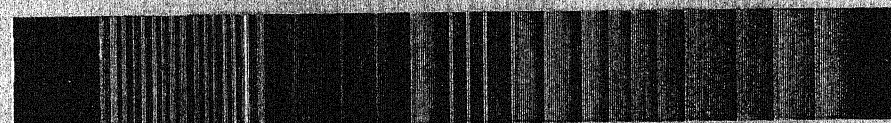
F<sub>1</sub>



E



D



C



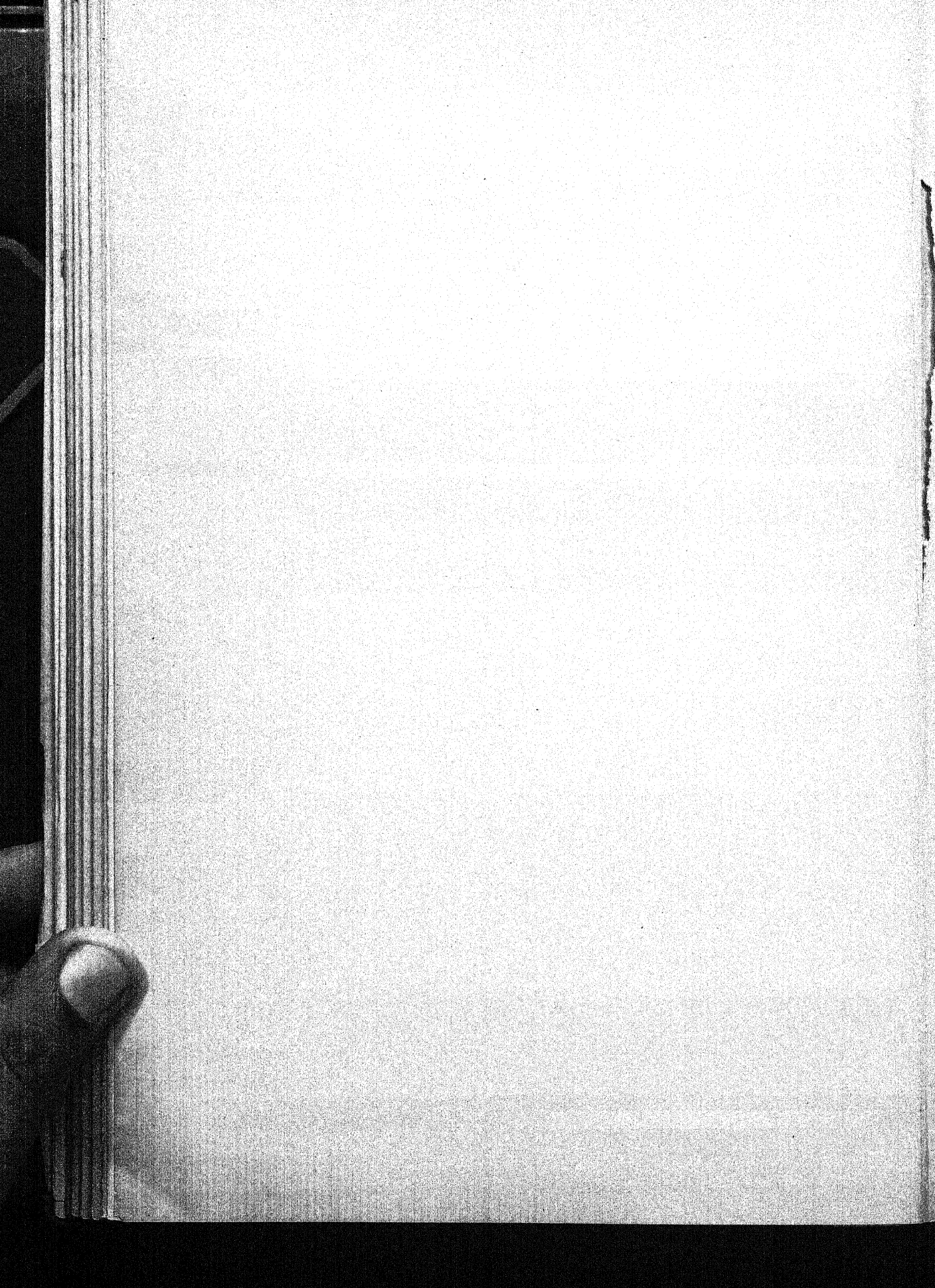
B



A

# SPECTRA OF THE ATMOSPHERIC GASES AND OF HYDROGEN

A, Hydrogen; B, Oxygen; C, Nitrogen; D, Helium; E, Neon; F<sub>1</sub>, Argon, red spectrum;  
F<sub>2</sub>, Argon, blue spectrum; F<sub>3</sub>, Argon, green spectrum; G, Krypton; H, Xenon.





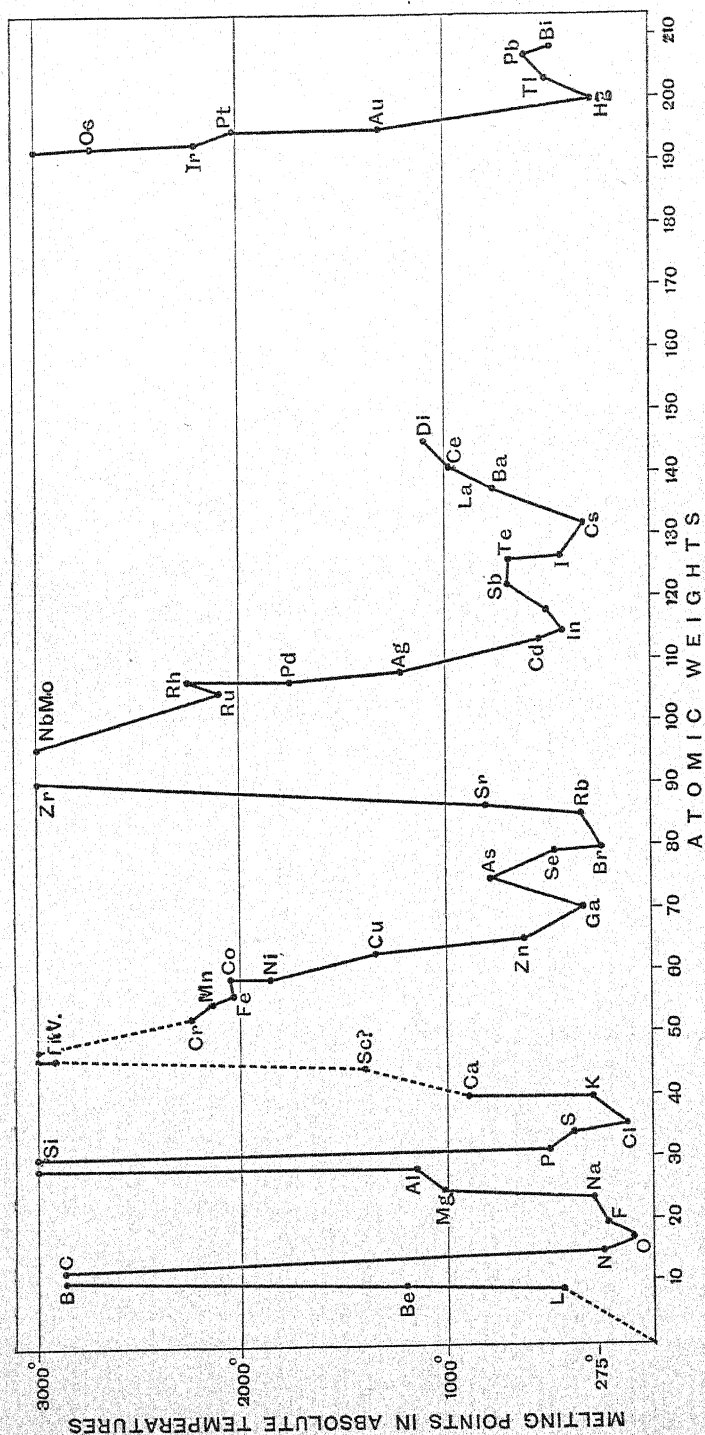


Fig. 50.—Curve showing Melting Points of the Elements and their relation to the Atomic Weights

cobalt; ruthenium, rhodium, and palladium; and osmium, iridium, and platinum—occur at the minima (lowest points). Again, calcium, strontium, and barium, which are closely allied, occupy similar positions on the descending portions of the curve. Other examples of the same nature can be found on examination, and all tend to confirm the view that the properties of the elements are periodic functions of the atomic weight.

**FUSIBILITY.**—A further illustration of this periodicity of physical properties is to be found in the fusibility. Meyer prepared a curve in which the ordinates are temperatures of fusion in degrees absolute and the abscissæ atomic weights.

A certain resemblance will at once be noticed between this curve and the one of atomic volumes. As the atomic weight increases, the melting-point rises and falls with a certain degree of regularity, so that maxima and minima are found as in the preceding curve. Generally speaking, elements which are fusible only with difficulty occupy positions on the descending branches of the atomic-volume curve, while those which are easily fusible or are volatile at the ordinary temperature are to be found on the ascending branches or at the maxima.

#### THE VALUE OF THE PERIODIC SYSTEM OF CLASSIFICATION

The value of such a system of classification as the one just described is not at first quite obvious. It is true that it provides a convenient method of arranging the elements in such a way that those most closely allied fall into groups, but beyond this it seems purely empirical. It has, however, been of considerable use in one or two ways, and these may be briefly considered here.

**FIXING ATOMIC WEIGHTS.**—In the first place, the periodic system has in several cases been of service in fixing the atomic weights of certain elements. It is frequently possible to determine with great accuracy the **EQUIVALENT** of an element. The equivalent is that number which represents the weight of an element which can combine with or replace one atom of hydrogen. The atomic weight must be some multiple of this number, and it has sometimes been a matter of difficulty to determine what this multiple is. For example, the equivalent of the element beryllium was found by Nilson and Petterson to be 4.54, and it was thought that the atomic weight was three times this value. If this is so, then in the periodic table it should come between carbon and nitrogen,



and stand at the head of the carbon group with the elements of which it has no affinities. This fact was pointed out, and the value 9 was given to the metal. Later, the atomic weight was determined by another method, namely that based upon the principle known as the law of Dulong and Petit, and the result justified the reasoning which had led to assigning the atomic weight 9 to beryllium.

By a similar process of reasoning, Mendeléeff came to the conclusion that the atomic weight 120 previously assigned to uranium was not correct, being only half the true value. He said that with an atomic weight of 240 uranium would occupy its proper position in the periodic table. This supposition has also been justified by more recent investigations.

One other instance in which the periodic system has been of use in fixing atomic weights may be given. This is the case of the so-called platinum metals. The atomic weights assigned to these elements were such that when the metals were arranged according to the plan of Mendeléeff they occupied the relative positions shown below:

Ruthenium	Rhodium	Palladium	Silver
Gold	Iridium	Platinum	Osmium

From a study of the properties of the different elements Mendeléeff came to the conclusion that the atomic weights were wrong, and that they should be such as would render possible the following arrangement:—

Ruthenium	Rhodium	Palladium	Silver
Osmium	Iridium	Platinum	Gold

The atomic weights were redetermined; that of gold by Thorpe and by Kruss, and those of osmium, iridium, and platinum by Seubert, with the result that the order suggested by Mendeléeff is now adopted.

PREDICTION OF NEW ELEMENTS.—A second, and perhaps at first sight a more striking, example of the possibilities of this generalization is that of the prediction by Mendeléeff of the existence of elements at the time unknown, and their subsequent discovery.

In Mendeléeff's table horizontal rows are known as SERIES and the vertical ones as GROUPS. On comparing the properties of an element it will generally be observed that they are the mean of the properties of its neighbours in the series and in the group. These neighbours were called by Mendeléeff the ATOMIC ANALOGUES, and it was from a consideration of these analogues that he was able to predict with wonderful accuracy the properties of the then unknown elements gallium, scandium, and germanium. To illustrate the method by which Mendeléeff arrived at

these results, we may take the case of SELENIUM and show how its properties are the mean of those of its atomic analogues.

Atomic Weights.			Density.			Atomic Volumes.		
	Sulphur 32			Sulphur 2.04			Sulphur 15.7	
Arsenic 75	Selenium 79	Bromine 80	Arsenic 5.67	Selenium 4.6	Bromine 2.97	Arsenic 13.2	Selenium 17.2	Bromine 26.9
	Tellurium 128			Tellurium 6.25			Tellurium 20.2	

EKA-BORON.—Mendeléeff in 1872 predicted the existence of an element which should come between calcium and titanium, and to which he gave the name EKA-BORON. This element, he said, would have an atomic weight of 44, would form an oxide ( $\text{Eb}_2\text{O}_3$ ) soluble in acids, and be more strongly basic than alumina and less basic than yttria ( $\text{Yt}_2\text{O}_3$ ). The oxide would have a density of 3.5 and would be insoluble in alkalis. The salts would be colourless, and would give gelatinous precipitates with caustic soda and with alkaline carbonates. With potassium sulphate it would form a double sulphate which would not be isomorphous with the true alums.

SCANDIUM.—In 1879 Nilson discovered a new element which he called SCANDIUM. On examination of its properties it was found that they were almost exactly the same as those of Mendeléeff's eka-boron. The oxide had the formula  $\text{Sc}_2\text{O}_3$ , and was a stronger base than alumina but weaker than yttria; scandium oxide was insoluble in alkalis and had a density 3.8. The salts were colourless and gave gelatinous precipitates with alkalis. A double sulphate having the formula  $\text{Sc}_2(\text{SO}_4)_3 \cdot 2\text{K}_2\text{SO}_4$  was prepared which was not isomorphous with the alums.

EKA-ALUMINIUM AND EKA-SILICON.—In similar terms Mendeléeff predicted the existence of an element between aluminium and indium, which he called EKA-ALUMINIUM, and of one between silicon and tin, provisionally named EKA-SILICON.

GALLIUM AND GERMANIUM.—The element discovered by Lecoq de Boisbaudran in 1875, and named by him GALLIUM, was found to be the predicted eka-aluminium, and GERMANIUM, discovered by Winkler in 1886, was Mendeléeff's eka-silicon.

Sufficient has been said to show that the periodic law is a great and useful generalization, but it must not be assumed that it is by any means perfect. As at present determined the atomic weight of tellurium is higher than that of iodine, whereas in consideration of its properties it should



have a lower value, so that it might be classed with sulphur and selenium. A large number of determinations have been made, but so far no certain proof has been brought forward to show that this is anything other than a marked exception to the general rule.

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## CHAPTER II

### THE GENESIS OF THE ELEMENTS—RADIO-ACTIVE SUBSTANCES

The periodic law seems to be a formal statement of some profound truth. As to the nature of this truth many speculations have not been wanting. Such striking regularities as are manifested by the elements in their physical and chemical properties must, it might be thought, be due to the presence of some substance common to them all, which itself recurs at intervals in varying proportions.

PROUT'S HYPOTHESIS.—If we except the early dreams of the alchemists, the first noteworthy expression of this view is to be found in what is known as Prout's hypothesis. This was propounded in 1815, and stated that all the elements had atomic weights that were simple multiples of that of hydrogen, and that in all probability all the elements were made up of hydrogen in various stages of condensation.

WORK OF STAS.—That this view of the nature of the elements is incorrect was shown by the accurate determination of atomic weights. First among those who by their labours succeeded in demonstrating the incorrectness of this hypothesis was Stas. In a masterly series of researches, extending over a period of forty years, he determined, with an accuracy hitherto unknown, the atomic weights of some ten or twelve elements. The result of his labours was the certainty that the hypothesis of Prout as originally stated was worthless, yet he started with the idea of proving its correctness. In his own words, written in 1860, he clearly makes this point obvious: "*Lorsque j'ai entrepris mes recherches, j'avais une confiance presque absolue dans l'exactitude du principe de Prout*".

At the present day most chemists agree in believing that the hypothesis of Prout is quite untenable, although, as Stas himself said, the approximation of the atomic weights to whole numbers is sometimes so close that "*il faut croire qu'il y a quelque chose la-dessous*".

The belief that there is "something" underlying the expression known

as the periodic law has tempted other chemists to speculate as to what this "something" may be. One of the most interesting of these attempts is that of Sir William Crookes.

CROOKES' HYPOTHESIS.—He supposes that the basis of all matter is a substance which he calls PROTYLE; from this, by a process of condensation, the elements, as known to us, have been formed. We may attempt to form a mental picture of the process of the evolution of the elements, and to do this it is necessary to look back to the time when the universe was in the nebulous state. At this time all was chaos, without form and void. The temperature was far higher than anything now conceivable. None of the planets had been thrown off from the central mass. Cooling gradually set in and the protyle condensed so that MATTER came into existence. The first element to appear was the one having the lowest atomic weight, and presumably the simplest structure, *i.e.* hydrogen.

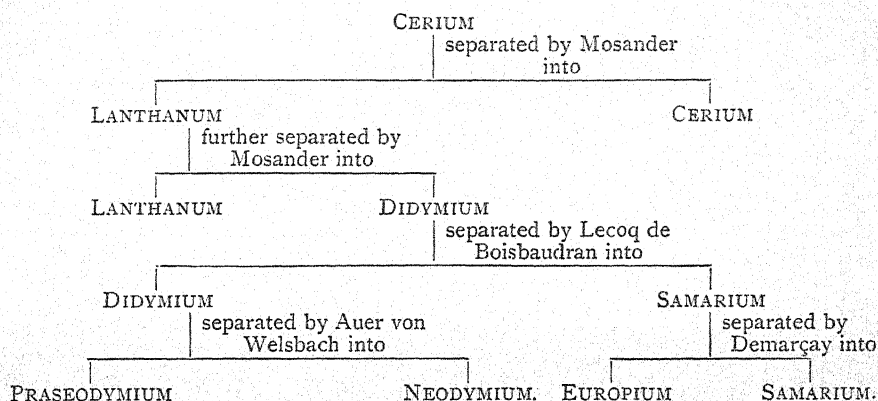
As the temperature continued to fall, other elements came into being, though a considerable gap in time must have occurred between the appearance of the two forms of matter. According as the rate of cooling was greater or less, so the properties varied. If the gap in time was lengthy, then the elements would differ widely in their properties; if short, then the elements would be closely allied. For example, carbon differs greatly from nitrogen, which succeeds it in order of atomic weight. This Crookes would explain by assuming a great interval of time between the birth of the two elements. On the other hand, there are certain groups of elements—such as iron, nickel, and cobalt; osmium, iridium, and platinum—in which the atomic weights lie very close to one another. In this latter case it must be supposed that the process of cooling at the time they made their appearance was very rapid, and in consequence they differ to only a slight extent from one another.

Eventually the temperature fell so low that the force which caused elements to be formed from protyle became more and more faint, until after the birth of uranium no more elements were formed.

This theory, though necessarily incapable of experimental verification, has much to recommend it. The idea of slow cooling causing the appearance of elements closely allied in properties receives some support when we consider the group known as the RARE EARTHS. These elements fall into two groups, those of the yttria series and those of the ceria series. By laborious processes of fractionation, substances formerly supposed to be elements have been separated into various constituents which have some claim to be regarded as true elements. In the following table are shown



the stages by which the original "element" CERIUM has been decomposed into five distinct "elements":—



A similar state of things is found in the case of the yttrium earths, for what were originally looked upon as two elements have since been resolved into no less than seven distinct elements. Nor is this the conclusion of the whole matter, for Crookes believes yttrium to be a mixture of at least five elements, while Kruss and Nilson state that "didymium" is made up of nine elements instead of the two found by von Welsbach. For these substances, so closely allied as to be only separable after a long series of fractionations, Crookes proposes the name META-ELEMENTS. These he regards as having been formed during a period of rapid cooling, so that they are not sharply differentiated from one another.

Pursuing the analogy of evolution still further, Crookes speaks of the birth, life, and death of the elements, of their struggle for existence, and the survival of those most fitted for their environment.

### RADIOACTIVE SUBSTANCES

Within the last few years a considerable amount of interest has been added to this question as the result of the discovery of the element RADIUM, for it seems that this is an element which is capable of transformation into others.

URANIUM AND THORIUM.—In 1896 Becquerel showed that URANIUM and its compounds possessed the property of giving out radiations which penetrated opaque objects and affected a sensitive photographic plate. Later, it was shown that the element THORIUM and its compounds showed the same phenomenon.

WORK OF MADAME CURIE, MARCKWALD, DEBIERNE, AND GIESEL.

—Madame Curie expressed the opinion that this was due to forces of an atomic nature, and attempted to support her view by experiment. She took a large quantity of pitchblende, obtained from the Joachimsthal in Bohemia, and separated it into its constituents by the ordinary processes of chemical analysis. It was found that the radioactive matter could be removed in three stages. The bismuth separated from the pitchblende contained a substance which was called POLONIUM, the barium a substance called RADIUM, and Debierne claims to have isolated a radioactive element which is precipitated with the rare earths.

After a long series of chemical processes, chiefly consisting of repeated crystallizations, Madame Curie succeeded in obtaining from one ton of pitchblende a small fraction of a gramme of radium chloride. With the radium salts prepared in this way practically all the investigations of the nature of this strange phenomenon have been carried out. Madame Curie did not succeed in separating polonium from bismuth to any great extent, though this was done by Marckwald in 1902. By most careful work he was able to obtain a preparation of the active matter, which, though infinitesimal in amount, was extraordinarily active. The amount obtained was only one-five-hundred-millionth part of the pitchblende with which he started.

The radioactive substance was called radio-tellurium by Marckwald, but it appears to be identical in all respects with the polonium of Madame Curie. In 1899 Debierne isolated a third active substance, to which he gave the name ACTINIUM, and this appears to be the same as the emanium described by Giesel.

#### THE PREPARATION OF THE RADIOACTIVE SUBSTANCES

The pitchblende is first broken into small pieces and roasted with sodium carbonate. The roasted mass is then extracted with hot dilute sulphuric acid. By this method the uranium passes into solution, while the bulk of the radioactive matter remains undissolved. The residue is acted upon with a strong solution of sodium carbonate, and the soluble carbonate so formed removed by washing. After this treatment the residual matter is extracted with hydrochloric acid, in which it is almost entirely soluble. The radium sulphate, however, remains for the most part undissolved.

This radium sulphate is again converted into carbonate by means of a saturated solution of sodium carbonate, and after careful washing is dissolved in hydrochloric acid.



The solution containing the actinium and polonium is neutralized with boiling caustic soda solution.

The residue remaining after this treatment is almost entirely soluble in cold hydrochloric acid, and from a solution in this acid polonium is precipitated with sulphuretted hydrogen, and the actinium with ammonia.

The chlorides obtained are then separated into the different groups according to the ordinary methods of qualitative analysis. The polonium is precipitated along with bismuth and smaller quantities of lead and copper. The sulphides are converted into a mixture of oxides and sub-nitrates, with nitric acid, and then fractionally precipitated with water. The bulk of the polonium is thrown down with the bismuth.

From among the elements precipitated by ammonia Debierne found an intensely active substance resembling thorium in properties. This was named actinium, and seems to be identical with the emanation substance described by Giesel.

The radium is thrown out along with the barium, and from the impure barium chloride thus obtained radium chloride is prepared by a process of fractional crystallization. This fractionation depends upon the fact that the radium chloride is less soluble in dilute hydrochloric acid than is barium chloride itself. An improvement on this, Madame Curie's method, is that suggested by Giesel, in which hydrobromic acid is substituted for hydrochloric acid.

The only one of the radioactive elements which has been thoroughly investigated as regards its chemical properties is radium. Madame Curie determined its atomic weight by precipitating a known weight with silver nitrate, and determining the weight of the silver chloride thus formed. The result upon which most reliance is to be placed gave a value of 225. This would suggest that radium occupied a position in the periodic table which included it in the group of the alkaline-earth metals. This is in accordance with its chemical properties, since in almost all respects it resembles barium. On the other hand, Runge and Precht have examined the spectrum of radium, and from a comparison of this with those of the other members of the alkaline-earth group, they have come to the conclusion that the atomic weight must be in the neighbourhood of 258. Up to the present time this apparent discrepancy remains unexplained, although greater trust must be placed in the figure given by Madame Curie, since this value has been recently confirmed by the work of Thorpe.

The method of investigation adopted by Becquerel was based upon the effect produced by the radiations on a photographic plate. This has been entirely replaced by another and far more delicate method introduced by

Rutherford. It depends on the fact that the radiations from radium and the other active substances possess, in common with the X-rays and the cathode rays, the power of converting gases through which they pass into conductors of electricity. It has been shown that no two of the radioactive elements behave alike in this respect, so it is possible to distinguish accurately between the different elements.

The peculiar feature of these substances is the emission of rays. So far three distinct kinds of these have been observed, and to them the names  $\alpha$ ,  $\beta$ , and  $\gamma$  rays have been given.

$\gamma$  RAYS.—These are characterized by a great power of penetration. Rutherford has shown that 1 per cent survive absorption after penetrating 150 cm. of water, 10 cm. of iron, or 7 cm. of lead.

$\beta$  RAYS.—These produce little ionization, but have great phosphorescent and fluorescent powers. It has been established that they are identical with the cathode rays.

$\alpha$  RAYS.—These, on the other hand, are characterized by their great ionizing power, slight penetrative power, and feeble photographic effect. If a screen of zinc sulphide is exposed to the influence of the emanations of a radium salt, it is seen that the screen becomes phosphorescent, and if this phosphorescence is examined with a lens it is seen to consist of a series of flashes. It is highly probable that each flash corresponds to an impact of a particle discharged from the radium.

TRANSFORMATION OF ELEMENTS—WORK OF RAMSAY, SODDY, AND CROOKES.—Not the least interesting of all the remarkable facts observed in connection with radioactive matter is that of the spontaneous change of radium into helium. Radium gives out an emanation which can be condensed. The condensed emanation was placed by Ramsay and Soddy in a spectrum tube, and special precautions were taken to remove all helium. Three days afterwards the bright-yellow line which is characteristic of helium was observed. Using the same quantity of radium, these observers succeeded in continuously transforming a portion of it into helium. This observation has been confirmed by other workers, so that there seems to be no doubt that one of the dreams of the alchemist has been realized, and matter is capable of transformation.

It has been shown that both uranium and thorium give out emanations which can be condensed. To these Crookes has given the names URANIUM X and THORIUM X respectively. They cannot be made to combine, and the suggestion has been made that they are of the nature of the recently discovered gases of the atmosphere. Crookes separated the uranium X from uranium, and found that the residual uranium was



quite inactive, but on keeping the uranium for a year it regained its activity. This leads to the conclusion that there is in the case of all the radioactive substances a continuous cycle of change.

Recent researches show that the process of change is an exceedingly complicated one. A large number of intermediate products has been observed, but one thing seems clear, namely, that thorium and uranium in particular are constantly undergoing transformation. It has been suggested by Rutherford that the  $\alpha$  particle emitted from radium is in reality an atom of helium, and Soddy states that he has observed the production of helium from uranium. If this be so, and there seems no reason to doubt the correctness of the statement, then we have evidence of the change first of uranium into radium, and then of the transformation of the latter into helium.

It is too early as yet to express any very decided views on the subject of this transformation of one element into another. We seem to stand on the verge of some new and great discovery, which may well revolutionize the whole of our present system of thought. Be that as it may, recent advances in this most fascinating branch of Natural Philosophy compel us to the view that, as Stas said, there may be "something" underlying Prout's hypothesis.

The early speculations of the early Greek philosophers, particularly those of Lucretius, are perhaps more interesting to-day than ever before.

"When the atoms part from a substance,  
That suffers loss: but another is gaining an increase:  
So that as one thing wanes, still a second bursts into blossom,  
Soon in its turn to be left. Thus draws this universe always  
Gain out of loss."

These words of Lucretius, old as they are, bear the impress of truth, and have for us a meaning far beyond that which they conveyed to him. It remains to be seen how far experiment will confirm these shrewd guesses as to the nature of matter.

#### A NEW CONCEPTION OF MATTER

**ELECTRON THEORY.**—During the last ten years or so an enormous amount of research has been carried out with the object of throwing fresh light on this vexed question as to the structure of matter, and in consequence of this an entirely new conception of the problem has arisen. Briefly, this conception is as follows: The atoms are no longer regarded as the "hard impenetrable particles" of Newton, but as spheres of positive

electrification containing electrons. The cathode rays from a Crookes tube behave as though they were particles charged with negative electricity, moving with a velocity of the same order as that of light. To these particles the name of ELECTRONS has been given. It is supposed, then, that these electrons arrange themselves round the centre of positive electrification under its influence and that of their own repulsion. They are never at rest, but in a state of constant motion round the centre of the "atom".

MAYER'S EXPERIMENTS.—An attempt to express this view in an experimental form was made by Mayer. The electrons are represented by little magnetized needles made to float on the surface of water by small pieces of cork, so that their negative poles are uppermost. The sphere of positive electrification is represented by a positive pole held over the magnets. The manner in which the magnets arrange themselves is shown in the following diagram.

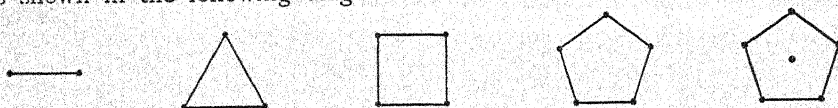


Fig. 51.—Diagram illustrating the Arrangement of a Number of Magnets under the Influence of a Sphere of Electrification

It will be noticed that when the number of magnets exceeds five, a new arrangement is necessary, and two systems are recognized. In this way we have some suggestion of the meaning of the periodicity of the elements, and it has been demonstrated mathematically that such a scheme can be elaborated so as to "explain" not only the periodicity of the elements, but also the phenomena of chemical forces, valency, &c.

LE BON'S VIEW.—On this view matter has not only been explained, but as a well-known statesman recently said, it has been explained away. We have seen that there is a transformation of one form of matter into another in the case of radium, and some scientists go so far as to state that this phenomenon is universal. Prominent among these is Gustave le Bon, who, in a book entitled *L'Évolution de la Matière*, has put forward these views in no undecided manner. He regards matter as being anything but inert. On the contrary, it is a reservoir of energy, which he calls the "intra-atomic energy". His conclusions may be briefly stated as follows.

Matter, which was formerly supposed to be indestructible, slowly vanishes because of the continuous dissociation of the atoms of which it is composed. During this dissociation of matter, or DEMATERIALIZATION as he calls it, substances are formed which are intermediate in



properties between so-called matter and the imponderable ether, between the two worlds which science has, up to the present, completely separated.

Heat, electricity, and the other forces of the universe are derived from the intra-atomic energy which appears when matter dissociates. Matter and force must therefore be looked upon as two different manifestations of the same thing—matter as a stable form and energy as an unstable form of the intra-atomic energy; and further, in the process of dematerialization of matter, force, in the shape of what we call electricity, heat, light, is developed.

According to these views, the atom, like the living forms with which we are acquainted, is born, experiences phases of growth and decline, and finally dies.

The little systems have their day and then cease to be. To the future must be left the further development of these views, the confirmation or denial of the truth of the saying: "*Rien ne se crée. Tout se perd.*"

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### CHAPTER III

## CHEMICAL COMBINATIONS

So far we have been concerned with matter solely as regards the atom. We have now to consider it from a different point of view—that is, from the point of view of the COMBINATIONS which atoms undergo. We have to consider the laws governing the formation of compounds, the arrangement of the atoms within the molecule, and the behaviour of compounds towards each other.

**MOST ELEMENTS CAN COMBINE.**—With the exception of the recently discovered gases of the atmosphere, *i.e.* helium, neon, argon, krypton, and xenon, all the elements possess the power of combination with other elements. There are certain rules underlying the combinations of atoms, and these we can here briefly consider.

**VALENCY.**—It has been found by experiment that an atom of chlorine combines with one atom of hydrogen, an atom of oxygen with two atoms of the same element, an atom of nitrogen with three atoms, and so on. This is expressed by saying that hydrogen and chlorine are MONOVALENT, oxygen DIVALENT, nitrogen TRIVALENT. Many attempts have been made to discover the law underlying this phenomenon, but so far without result. The question is further complicated by the fact that valency

is apparently a variable quantity. For example, phosphorus forms two compounds with chlorine, one represented by the formula  $\text{PCl}_3$  and the other by the formula  $\text{PCl}_5$ . Carbon is almost universally tetravalent, but in one compound, carbon monoxide, it seems to be divalent. One of the most remarkable examples of this variable valency is seen in the case of a compound known as diphenyl iodonium iodide. This contains two atoms of iodine, one of which is monovalent, while the other is trivalent.

In almost all its compounds carbon is tetravalent. An exception to this has already been mentioned, namely, that of carbon monoxide; but quite recently a compound has been discovered in which carbon appears to be trivalent. For all practical purposes, however, we may consider these two cases as quite exceptional, and not introduce them into the present discussion.

**CARBON COMPOUNDS.**—The element carbon is unlike the other elements in that it possesses the property of forming an almost infinite number of compounds with hydrogen, oxygen, and nitrogen. In fact, the whole subject known as **ORGANIC CHEMISTRY** is concerned with the study of these compounds. This vast subject is, for purposes of convenience, subdivided into main branches, the chemistry of the fatty compounds and that of the aromatic compounds.

**FATTY AND AROMATIC COMPOUNDS.**—In the first-named class are included substances which are related to naturally occurring compounds derived from the fats. To the second class belong compounds allied to various aromatic-smelling substances, such as oil of bitter almonds, gum benzoin, &c. This classification is, of course, only arbitrary, but after close examination of the nature of the compounds it is found that this division is a useful one.

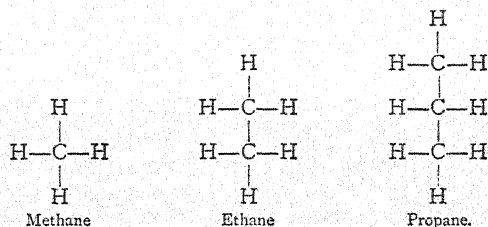
It is supposed that in the fatty compounds the carbon atoms are arranged in the form of an open chain, while in the aromatic series the atoms are regarded as being linked so as to form a ring.

**HYDROCARBONS—PARAFFINS.**—In the ordinary petroleum of commerce there has been found a large number of substances known collectively as **HYDROCARBONS**. These are made up of carbon and hydrogen only, and amongst them are bodies which are called **PARAFFINS**. These are closely allied in chemical properties, so closely, indeed, that they are said to belong to an **HOMOLOGOUS SERIES**. That is to say, they can be prepared by similar methods, behave in a similar manner towards reagents, and exhibit a gradation in properties as the series is ascended. The lowest member of the series is a gas, **METHANE**, or marsh gas as

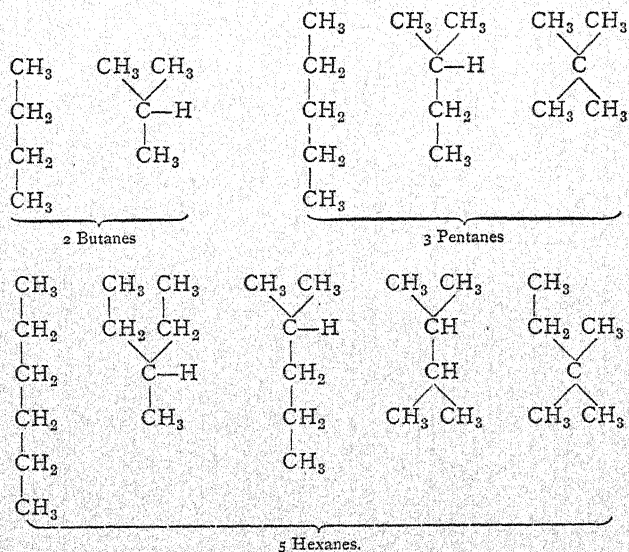


it is frequently called. Then follow in order of increasing molecular weight, ETHANE, PROPANE, BUTANE, PENTANE, HEXANE, &c.

The formulæ assigned to these are  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ , and  $\text{C}_5\text{H}_{12}$  respectively, and it will be noticed that each differs from the one preceding it by a constant difference of  $\text{CH}_2$ . It is usual to represent these compounds by what are known as GRAPHIC FORMULÆ, which are drawn up on the assumption that carbon is tetravalent. For the first three members of the series the following formulæ are accepted:—



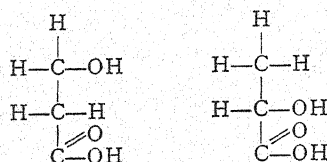
In the case of the other members of the series there are possible *alternative* methods of representing the structure. For example, we can write the formulæ for butane in two, for pentane in three, and for hexane in five different ways. Moreover, to lend support to the theoretical possibility, it is found that compounds corresponding to these formulæ are known.



These different forms of the same compound are called ISOMERS, or ISOMERIDES, and the phenomenon of which they are examples is known as ISOMERISM. This is not confined solely to the hydrocarbons, but is

found amongst many of their derivatives, such as acids, alcohols, ethers, &c.

LACTIC ACIDS.—As an illustration of this we may take the case of the lactic acids. From theoretical considerations we should expect to find two modifications having the formulæ—



respectively. This expectation is fully justified, for it has been proved by synthesis that two different acids having the above formulæ do

actually exist. In addition to these acids prepared synthetically, there is another which has the same composition, and is in all respects save one identical with the second of the two above mentioned.

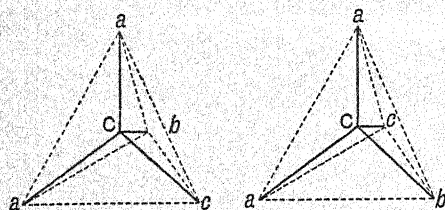


Fig. 52.—Diagrams representing the Arrangement of Different Groups round the Centre of a Regular Tetrahedron

account for this some hypothesis is needful, and this was provided when van't Hoff and le Bel, in 1874, propounded the view that it was necessary to take into account the arrangement of atoms in space. Lactic acid occurs naturally as the result of the acid fermentation of milk, and also as a constituent of meat juices. The acid formed artificially is identical with that obtained from milk, but differs from that found in meat extracts in one important respect. The latter turns the plane of a ray of plane-polarized light to the right, while the former has no such effect.

A similar state of affairs was found by Pasteur to exist in the case of the tartaric acids, but the cause was not understood until after the enunciation of le Bel and van't Hoff's hypothesis of the spatial arrangement of atoms. It was suggested independently and almost simultaneously by these two chemists that the carbon atom might be regarded as a regular tetrahedron, or rather that the atom could be regarded as being situated at the centre of a tetrahedron with its linkings directed towards the four corners. In the above figures (fig. 52) the carbon atoms are represented as linked to four groups, two of which are the same. It will be seen

HYPOTHESIS OF LE BEL AND VAN'T HOFF.—Evidently to



that it is possible to superpose one upon the other so that they may each be made to represent the same compound.

If, on the other hand, the four groups are all different (fig. 53), then it will be found quite impossible to superpose the two, and all that can be done is to turn the one form so that it becomes the mirror image of the other.

On applying this method to the lactic acids we have the following graphic representation:—

If it be assumed that fig. 54A is the configuration of sarcolactic acid (the one found in meat extracts), then fig. 54B should be the configuration of another isomer, or,

since we are dealing with spatial considerations, a STEREOISOMER. By a method to be described later, the synthetic lactic acid has been resolved into two forms, one of which rotates the plane of polarization to the right, DEXTROLACTIC ACID, while the other, LÆVOLACTIC ACID, rotates the plane to the left to exactly the same amount as the former did to the right. On mixing equal quantities of the two stereoisomers, it is found that the mixture has no effect on the plane of polarized light, and is identical in

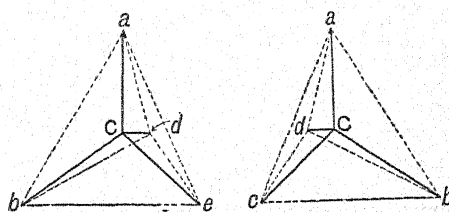


Fig. 53.—Diagrams representing Asymmetric Carbon Compounds

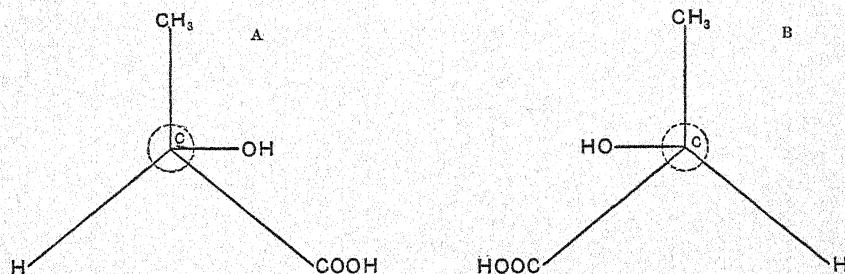


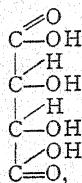
Fig. 54.—Lactic Acids represented as Stereoisomers

all respects with fermentation lactic acid, and with the one obtained as the result of synthesis.

ASYMMETRIC ATOMS AND OPTICALLY ACTIVE COMPOUNDS.—On examination of other compounds which rotate the plane of polarized light, or, as they are called, optically active compounds, it is found that they all contain a carbon atom united to four different groups or atoms. Such a carbon atom is said to be ASYMMETRIC, and so far as has been ascertained every optically active compound contains at least one asymmetric carbon atom. The converse of this statement, however, is not

universally true, for some compounds which undoubtedly contain an asymmetric atom are not optically active.

TARTARIC ACIDS.—The reason for this will be seen when we examine the case of the tartaric acids. The structural formula for tartaric acid is—



and on attempting to represent all possible configurations it is found that there are three (fig. 55). It is more convenient, however, to make

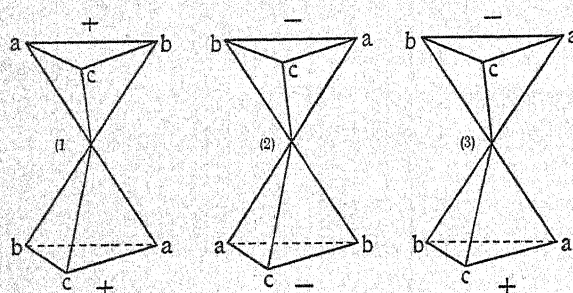


Fig. 55.—Stereo Arrangement of the Tartaric Acids

a plane projection (fig. 56), where (1), (2), and (3) of fig. 55 become (4), (5), (6) respectively. The intersections of the horizontal and vertical lines represent carbon atoms.

It will be noticed that the compound represented by (4) is the mirror image of that represented by (5), and consequently if we assign (4) to DEXTROTARTARIC ACID we must look upon LÆVOTARTARIC ACID as represented by (5), since the one behaves towards polarized light in exactly the opposite sense to the other. In formula (6) there is a plane of sym-

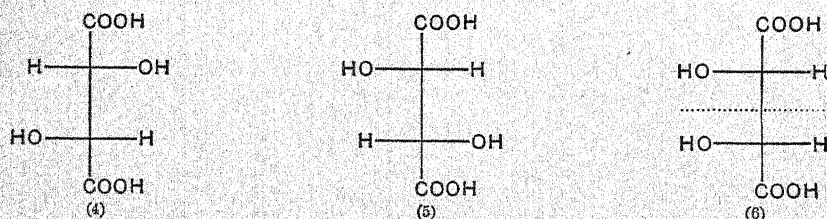


Fig. 56.—Plane Projections of the above

metry in the molecule indicated by the dotted line. This plane divides the molecule into two halves, each of which bears the same relation to the other as an object does towards its image in a mirror. Accordingly if we assume the rotatory effect to be due to an influence exerted by the different parts of the molecule, then we might reasonably expect to



find that there was an acid having the structure represented by formula (6) which was optically inactive.

**RACEMIC ACID AND MESOTARTARIC ACID.**—In actual fact it is found that *four* modifications of tartaric acid exist, two of which are optically active and two inactive. The two which are active are, of course, the dextro and the laevo acids, and if equal quantities of these be taken, dissolved in water, and the solution allowed to crystallize, a product is obtained which is optically inactive, and is in all respects similar to the acid prepared synthetically. This acid is called **RACEMIC ACID**. When dextrotartaric acid is heated for several hours with a solution of caustic potash a new form of tartaric acid is produced, and this too, like racemic acid, is optically inactive. It is known as **MESOTARTARIC ACID**, and is quite different from the racemic form in physical characters. The most interesting respect in which it differs is this: racemic acid can, by suitable methods, be resolved again into the two optically active forms from which it was built up. Mesotartaric acid, on the other hand, cannot by any known means be resolved into two active constituents. In the former case the optical inactivity is due to the counterbalancing of the effect due to one molecule by that due to the other, a case of external or *intermolecular* compensation, whereas mesotartaric acid is optically inactive because the one half of the molecule balances the other half, a case of internal or *intramolecular* compensation.

**RESOLUTION OF RACEMIC ACID.**—It was mentioned above that the racemic form could be resolved into its optically active constituents. To effect this change there are applicable three methods, all of which are due to Pasteur.

Optically active isomers, rotating the plane of polarization in opposite directions, show no difference in their chemical and physical properties, such as solubility, melting-point, and boiling-point. Their salts crystallize in the same manner, with the same number of molecules of water of crystallization, so that it is obviously impossible to attempt to separate them by the ordinary means. The three methods by which they may be separated are given below.

1. On crystallizing a solution of certain salts of racemic acids it is found that the crystals are of two forms, one corresponding to the dextro and one to the laevo form. For example. Pasteur found that a solution of sodium ammonium racemate on crystallization yielded two kinds of crystals, which were related to one another as an object and its mirror image. These he succeeded in picking out under the microscope, and found that the one kind gave a dextrorotatory solution, while the other

was as strongly lævorotatory. The crystals of the two acids possess what are known as *hemihedral* faces, which are shown dark in the accompanying figure. They form mirror images of one another (fig. 57).

2. Although the salts of racemic acids behave similarly towards symmetrical bases such as potash, soda, or ammonia, yet if the acids be treated with an optically active, and therefore asymmetric, base like strychnine or cinchonine, one of the isomeric salts differs in solubility from the other, so that by fractional crystallization of the mixture it is possible to separate the mixture into its optically active constituents. By this method, using cinchonine, Pasteur was able to resolve racemic acid into dextro- and lævotartaric acids.

3. When a dilute solution of racemic acid is inoculated with the green-mould fungus (*Penicillium glaucum*) the optically inactive solution gradu-

ally becomes lævorotatory, since the mould grows principally at the expense of the dextrorotatory form. It was formally supposed that the lævo form was entirely unattacked, but subsequent research has shown that both forms are attacked

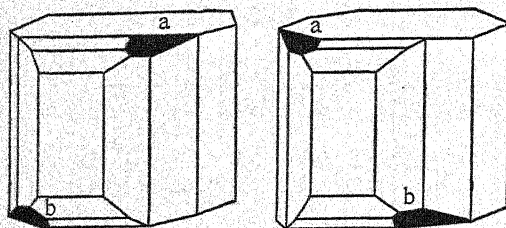


Fig. 57.—Crystals of Dextro and Lævo Sodium Ammonium Tartrates showing Hemihedral Faces

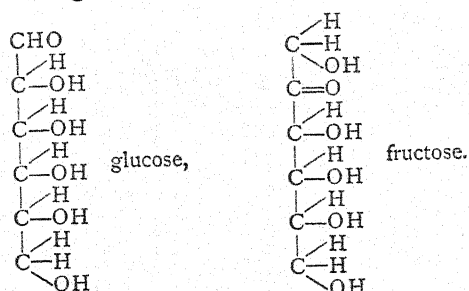
simultaneously, though the one is preferred to, and is destroyed more rapidly than the other.

One of these three methods is applicable to all cases of racemic compounds, though where the substance is a base an acid of similar structure must naturally be used instead of an optically active base. In case the substance under investigation is neither an acid nor a base it is necessary to convert it into one or the other, resolve the mixture, and then from the active compound again derive the corresponding substance in its active form.

**HEXOSE SUGARS.**—Perhaps the most interesting of all the examples of stereoisomerism is to be found in the case of a class of compounds known as the **HEXOSE SUGARS**. The first product of oxidation of an alcohol is an **ALDEHYDE**, a substance containing the group  $\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{O} \end{array}$ . A sugar is defined as an aldo- or keto-alcohol, and the hexose sugars are those containing six carbon atoms. The best known of these are **GLUCOSE** or grape sugar, and **FRUCTOSE** or fruit sugar. These have the same composition, but it has been established that while glucose



contains an aldehyde group, fructose contains a ketone group. The structural formulæ assigned to these are as follows:—



In glucose there are four asymmetric carbon atoms and in fructose three, so that we might reasonably expect to find that there were a considerable number of stereoisomers. This supposition is justified by experience, for no fewer than eleven isomers of glucose are known.

EMIL FISCHER'S WORK.—It is highly improbable that the mystery of the sugar group would ever have been unravelled but for the discovery by Emil Fischer of the behaviour of these compounds towards phenyl hydrazine. With this substance all the hexoses form compounds by means of which it is possible to identify the original sugar.

Fischer found that glucose, mannose, and fructose gave the same OSAZONE (the compound with phenyl hydrazine), therefore the configuration of three of the asymmetric carbon atoms must be the same in the three sugars. By a lengthy and complicated process of reasoning he determined that the configuration of these three sugars must be as follows (fig. 58):—

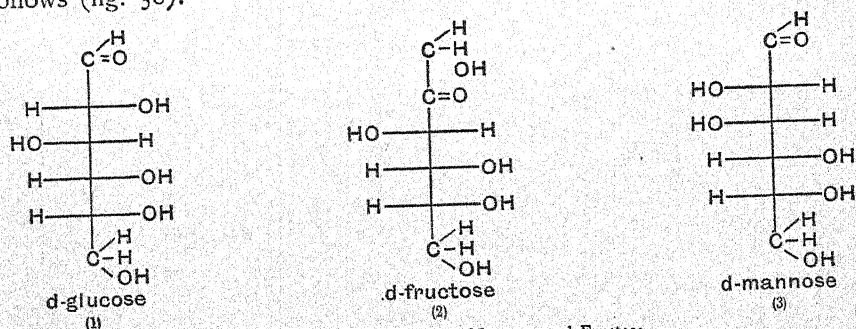


Fig. 58.—Formulæ of Glucose, Mannose, and Fructose

He further assumed that the formula (1) was that of d-glucose, and upon this basis he was able to assign formulæ to all the sugars derived from glucose. In addition to these he prepared other sugars containing

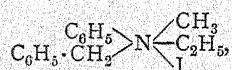
seven, eight, and nine carbon atoms, and by the degradation of the hexoses sugars containing five, four, three, and two carbon atoms.

In all cases theoretical considerations have been fully borne out by experience, and Fischer's work remains as one of the most striking examples of the confirmation of an hypothesis at first regarded as almost untenable, but which has since proved of extraordinary value to the science.

### STEREOISOMERISM DUE TO ELEMENTS OTHER THAN CARBON

**SULPHUR, SELENIUM, AND TIN.**—Carbon is not the only element the compounds of which show this phenomenon of stereoisomerism, for in 1900 Smiles was successful in preparing a compound containing an asymmetric sulphur atom which he resolved into its optically active constituents. Similarly Pope and Neville resolved a compound containing an asymmetric selenium atom, and a little later Pope and Peachey prepared a substance, tin methylethylpropyl iodide, from which they separated an optically active form.

**NITROGEN.**—This is another element which is capable of giving stereoisomers, but only when it possesses a valency of five. Trivalent nitrogen shows no asymmetry. Pope and Peachey prepared two compounds having the composition phenylbenzylallylmethyl ammonium iodide. It was found that if allyl iodide was added to methylbenzylaniline a different compound was formed from the one produced by the addition of methyl iodide to allylbenzylaniline, although both contained the same groups. This fact points to a difference between the five affinities of the nitrogen atom. Another compound, phenylbenzylmethylethyl ammonium iodide,



was prepared by Jones, and resolved by him into optically active forms.

### GEOMETRICAL ISOMERISM

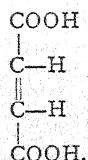
There remains yet to be considered another form of isomerism, due to the arrangement of atoms in space, and to this the name of GEOMETRICAL ISOMERISM may be given. Many cases of this are known, but only one or two examples will be here given.

**MALEIC AND FUMARIC ACIDS.**—When malic acid is distilled there



results a mixture of fumaric acid and maleic anhydride. On the addition of water to the anhydride, maleic acid is formed. Maleic and fumaric acids differ in many respects, yet both have the same percentage composition and possess the same structure, since they can both be reduced to the same acid. Here then we have an example of a form of isomerism quite different from any with which we have hitherto become acquainted. For a long time the matter remained a mystery, until an explanation of the case was provided by Wislicenus.

Both maleic and fumaric acids must possess the structure represented by the formula—



As carbon is (almost) universally tetravalent, two of the carbon atoms must be connected by a double bond. This double bond, if we use the tetrahedron to represent the carbon atom, must arise from the deflection of two of the linkings, so that the tetrahedra are joined, not by their apices, as in the case of the tartaric acids, but along one edge. Assuming this, we have the following graphic representation of the structure of the two acids (fig. 59):—

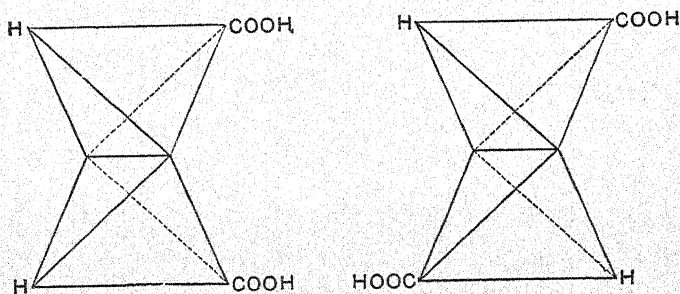
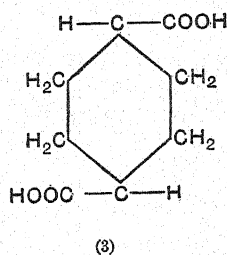
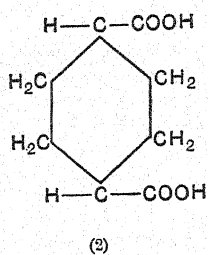
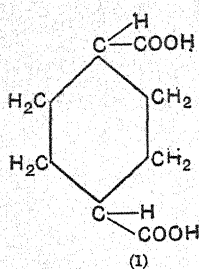


Fig. 59.—Formulae of Maleic and Fumaric Acids

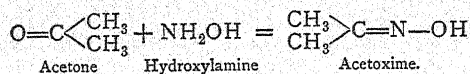
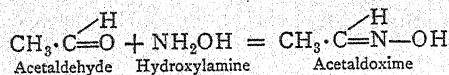
If this supposition be correct, then it is easy to assign the first formula to maleic acid, because the two COOH groups are in proximity, and water would be split off more easily to form the anhydride than in the other case, where the COOH groups are on opposite sides of the molecule.

A similar case of isomerism is to be found in HEXAHYDROTEREPHTHALIC ACID, which has the formula (1).

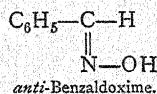
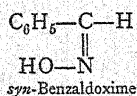


Two acids are known, one of which gives an anhydride, while the other does not. Consequently formula (2) is assigned to the one which loses water, and formula (3) to the other modification.

OXIMES.—Another interesting example of this kind of stereoisomerism is found in the case of certain compounds known as oximes. These are formed by the action of hydroxylamine on aldehydes and ketones according to the following equations:—



It was observed that in the case of benzaldehyde two isomeric oximes were formed, and the existence of these could only be explained by assuming that the isomerism was of the spatial kind. The two forms may be represented in a plane configuration in the following manner:—



The one in which the phenyl group is adjacent to the hydroxyl group is called the *syn* form, and the other the *anti* form.

Many other examples of this form of isomerism are known, but those already given will be sufficient to illustrate the phenomenon. In conclusion, it may be mentioned that some of the compounds of platinum and also of cobalt exhibit isomerism, which some workers have sought to explain by having recourse to a theory of the spatial arrangement of the atoms; but as the matter is an obscure one, and by no means definitely settled, we cannot here discuss the question.



## CHAPTER IV

### STATES OF MATTER

**THREE STATES OF MATTER.**—Matter as revealed to the senses occurs in three different forms—solid, liquid, and gaseous. Under certain conditions a given substance can pass from one to another of these states, as is seen in the familiar case of water. In the form of ice, liquid water, and steam we have the three states of matter exemplified. As previously stated, it is usually supposed that in the solid state the particles are placed much more closely together than in the liquid state, and move with much more friction. Further, in the state of liquid the particles are in a state of greater concentration than in the gaseous, but less than in the solid state. It would therefore seem possible to convert matter from the gaseous first to the liquid and then to the solid states, and as a matter of fact this can be done in almost every case.

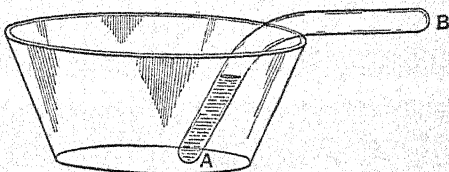


Fig. 60.—Faraday's Apparatus for the Liquefaction of Gases

**FARADAY'S LIQUEFACTION EXPERIMENTS.**—The earliest work on the liquefaction of gases was done by Faraday, who lowered the temperature and increased the pressure simultaneously. This he was able to do in certain instances by the use of the following device. A compound which on heating gave off the gas it was desired to liquefy was sealed up in a tube of the form shown in fig. 60. The lower end, A, was placed in a freezing mixture, and the other end, B, contained the compound heated. In this way the internal pressure was increased and the gas given off cooled at the same time, so that it condensed in the lower limb.

Chlorine was liquefied in this way by using a compound formed when the gas is passed into ice-cold water, ammonia by using a compound with silver.

There were some gases, however, to which this method was not applicable, and in consequence a different process for their liquefaction had to be devised.

**LAWS OF LIQUEFACTION.**—For every gas there is a certain temperature below which it may be converted into the liquid state, and above which no increase of pressure is capable of bringing about this change. This is spoken of as the **CRITICAL TEMPERATURE**, and the pressure which

at this temperature is just sufficient to convert the gas to liquid is the CRITICAL PRESSURE. Under these conditions the substance has a certain density, the CRITICAL DENSITY, and the reciprocal of this is the CRITICAL VOLUME. If, then, we can lower the temperature of a gas to the critical point, a slight increase of pressure will be sufficient to bring about liquefaction, and to achieve this end one of two methods is usually employed. The first is to cool the gas to as low a temperature as possible, and then to allow it suddenly to expand. In expanding, work is performed, and to supply energy for this work heat must be absorbed from the gas, and in consequence a portion of it is liquefied. The other method consists in

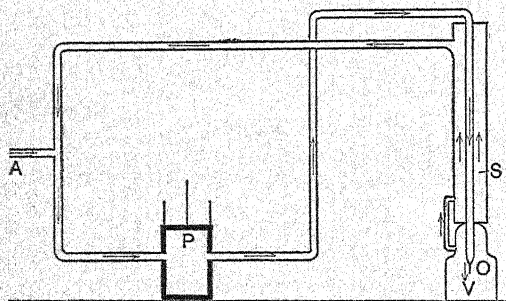


Fig. 6r.—Diagram of Apparatus for Liquefaction of Gases

allowing the gas to pass from a high pressure to a lower one through a porous plug. In this way the temperature is lowered, and by the repetition of the process the gas can be cooled to its critical temperature. This being accomplished, by a slight increase of pressure the gas gradually passes into the liquid state. In the accompanying diagram of the apparatus used (fig. 6r), the gas

passes in at A, is compressed by the pump P, and follows the direction of the arrows. At the outlet O it expands, and is thereby cooled. The cooled gas passes back through the annular space S, and serves the purpose of still further cooling a fresh quantity of gas. Eventually the temperature falls to the critical point, and liquid escapes at the nozzle O, and is collected in the vessel V.

WORK OF DEWAR.—By the use of this method Dewar succeeded in liquefying all gases which had previously resisted liquefaction, with the exception of helium. This element has, however, recently (1908) been liquefied by Kammerlingh Onnes. By causing liquid hydrogen to evaporate, exceedingly low temperatures have been attained. Hydrogen itself boils at a temperature of  $-253^{\circ}$  C. or  $20^{\circ}$  absolute. When helium is strongly cooled, and then allowed to expand suddenly, a temperature of  $9^{\circ}$  or  $10^{\circ}$  absolute is obtained. At these low temperatures the properties of bodies are very different from those observed at higher ones. Metals become more magnetic, substances like ivory and cotton wool are phosphorescent, crystals of uranium nitrate and other compounds are self-luminous. Indiarubber becomes so brittle that it may be reduced to a



state of powder in an ordinary mortar. Metals and other bodies become much more elastic, as shown by a simple but striking experiment. A piece of lead wire is coiled into the form of a spiral, and cooled to the temperature of liquid air. A heavy weight is suspended by the spiral, and so long as the wire is at a very low temperature it can support the weight. When, however, the temperature is allowed to rise, the spiral gradually straightens out and eventually the lead wire breaks.

ORGANISMS AND LOW TEMPERATURES.—Some interesting results regarding the behaviour of living organisms at these extreme temperatures were obtained. Certain bacteria which possess the property of phosphorescence were cooled down until the phosphorescence disappeared, and maintained at this temperature for a considerable time. On again allowing the temperature to rise, they once more became phosphorescent, thus proving that the vitality was not destroyed by exposure to great cold.

The relations existing between a substance in the three states of matter call for consideration, and will be briefly treated here.

LAWS OF BOYLE AND GAY-LUSSAC.—As is well known, the volume of a gas is influenced by both temperature and pressure. Boyle's Law states that the volume of a gas is inversely proportional to the pressure, and the law of Gay-Lussac that the volume increases by one two-hundred-and-seventy-third for a rise of  $1^{\circ}$  C. These two laws may be stated as one in the form of what is usually known as the *general gas law*. If we denote the pressure by  $p$  and the volume by  $v$ , and the absolute temperature by  $T$ , then the law reads—

$$pv = rT,$$

where  $r$  is a constant depending upon the nature of the gas.

DEGREES OF FREEDOM.—There are thus three variable magnitudes in the equation, namely, temperature, pressure, and volume. It is only possible, however, to fix in an arbitrary manner two of these, for if the pressure and volume be fixed, then there is only one temperature possible at which the conditions of the equation can remain valid. This is usually expressed by saying that the gaseous state has 2 degrees of freedom.

Similarly liquids and solids each have 2 degrees of freedom, so that we may state as a general principle that every simple body, solid, liquid, or gaseous, possesses 2 degrees of freedom both as regards its variability in volume and its variability as regards the influence of heat. This can be conveniently expressed in the form of a curve, such as the accompanying one, shown in fig. 62.

In this curve the ordinates represent pressures and the abscissæ temperatures. The curve  $OA$  represents the vapour-pressure curve of water. That is to say, at each point corresponding to a definite temperature and pressure, liquid water is in equilibrium with water vapour. The curve  $OB$  represents the vapour pressure of ice, and the curve  $OC$  shows the influence of pressure on the melting-point of ice. At  $O$  ice, liquid, and water vapour can coexist, and are all three in equilibrium. This point is called a **TRIPLE POINT**, and it is clear that for a substance which can exist in three phases only there can be only one such point.

From this diagram we find that the following state of affairs exists. At the triple point  $O$  all three phases can co-exist. Along the curve  $OA$

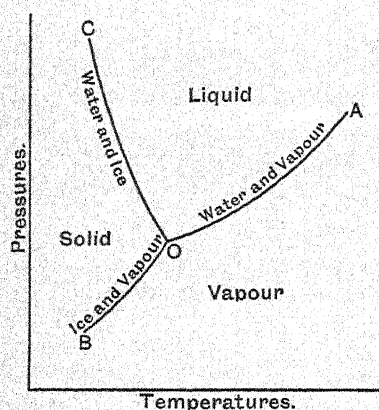


Fig. 62.—Diagram representing Equilibrium between the Three Phases of Water

two phases are in equilibrium, water and water vapour. Along  $OB$  ice and water vapour, and along  $OC$  water and ice are in equilibrium. In the region  $AOC$  only liquid water can exist, and in the regions  $AOB$  and  $BOC$  only vapour and ice respectively can exist.

This is the simplest case which can occur. Where there is more than one component the phenomenon becomes more complicated. For example, if we take the case of a solution of salt there are two components, and we have to introduce a third variable, namely, concentration.

Thus the liquid phase may be either pure water or it may be a solution of salt of a given strength. Fortunately, however, we have a convenient rule by means of which we can understand such cases theoretically. This is known as the **PHASE RULE**, which was developed by Willard Gibbs. It may be stated in the following form.

**PHASE RULE.**—If the number of phases exceed the number of components by two the system has no degree of freedom and is said to be nonvariant. If the number of phases exceed the number of components by one, the system has one degree of freedom and is monovariant. If the number of phases is equal to the number of components, the system has two degrees of freedom, and is divariant.

Let us consider this rule as applied to the case of water, using the diagram given above (fig. 62). The triple point  $O$  represents equilibrium between three phases. Neither the temperature nor the pressure can be varied without disturbing the equilibrium, for it is only at this point that



solid, liquid, and vapour can co-exist. The point O therefore represents a nonvariant system. In the case of the curves OA, OB, and OC we have examples of monovariant systems, for, providing we keep along the curves, we can vary either the temperature or the pressure without destroying the equilibrium. In the areas AOB, AOC, and BOC we have examples of divariant systems, for both the temperature and the pressure may be varied without the appearance of a new phase. If we represent the number of phases by  $p$ , the number of components by  $c$ , and the degrees of freedom by  $F$ , we can express the rule thus:

$$c + 2 - p = F.$$

MIXED SOLUTIONS.—The phase rule has been of use in solving many problems, one of the most important of which is the behaviour of mixed solutions of salts. Here there are of course several components, but by the application of the rule it is possible to determine what mixtures will separate under given conditions. In this way van't Hoff has been able to ascertain to some extent the conditions under which the enormous deposits of salts found at Stassfurt were formed.

ALLOYS.—One other case in which the phase rule has been of service is that of alloys. By its application to the study of these compounds much light has been thrown on this important subject, and the sum of our knowledge is greater than it would have been had this principle not been enunciated.

### THEORY OF SOLUTION

The phenomena of solution have of recent years been studied with so much assiduity that we are now in possession of an exceedingly large number of facts. From these, certain generalizations have been made which are of great interest and of considerable importance. In the following brief account some of the more important results will be given.

DIFFUSION OF GASES.—GRAHAM'S LAW.—As is well known, gases possess the power of dissolving one another, and this is usually spoken of as diffusion. The most important investigation of this question was carried out by Graham, who established a law that bears his name. This states that gases diffuse with a velocity which is inversely proportional to the square roots of their densities.

DIFFUSION OF SOLIDS.—Solids, too, possess the property of mutually dissolving each other, though the process is much slower and more limited than in the case of liquids or gases. That this should be so is not surprising, if we regard the particles of which they are made up as being

in the one state comparatively close together, while in the other state they are more widely separated, and so capable of moving about with a far greater velocity. A striking example of the diffusion of metals is to be found in some experiments carried out by Roberts-Austen. Discs of gold were carefully cleaned and then clamped to the bases of cylinders of lead. They were allowed to remain in a cellar for four years, and at the end of that time it was found that the discs had adhered, and on cutting slices from the lead cylinders at right angles to the axes it was seen that the gold had penetrated to a depth of 8 mm. into the lead. Another instance of this phenomenon of solid solutions is seen in the case of a compound which hydrogen forms with palladium. This metal can take up more than 800 times its own volume of hydrogen, and it is now generally believed that this is a case of solid solution,

### SOLUBILITY

The solubility of a substance may be defined as the quantity of SOLUTE (that is the substance dissolved) required to saturate a given amount of SOLVENT.

**SOLUBILITY OF GASES IN SOLIDS.**—Certain metals, such as platinum and palladium, possess the property of absorbing gases. This has been investigated by many observers, and the conclusion has been reached that in some cases true chemical compounds are formed, while in others we have examples of the phenomenon known as solid solutions.

**SOLUBILITY OF GASES IN LIQUIDS.**—In this case there are two possibilities. Sometimes, as in the case of a solution of hydrochloric acid in water, the gas cannot be completely expelled even though the pressure be lowered and the temperature raised. In other cases, as for example in solutions of oxygen and air, the gases can be entirely removed by the application of one or both these methods. As long ago as 1803 Henry showed that the mass of a gas dissolved by a liquid varied as the pressure. This means, since the volume is inversely as the pressure, that a liquid always dissolves the same volume of a gas. This law has been tested by later observers, and it has been ascertained that, while true in the main, it does not hold for very soluble gases such as ammonia and hydrochloric acid.

**SOLUBILITY OF LIQUIDS IN LIQUIDS.**—There are three classes into which pairs of liquids can be divided. 1. The liquids are mutually soluble in all proportions. 2. The liquids are soluble, but only to a limited extent. 3. The liquids are insoluble in each other.



**SOLUBILITY OF SOLIDS IN LIQUIDS.**—This phenomenon is as a rule only slightly affected by pressure, but more largely by temperature. Generally speaking, the solubility increases with rise of temperature, though there are exceptions to this, as in the case of calcium hydroxide and calcium citrate. This influence of temperature is sometimes of great importance in industrial processes. For example, the bulk of the potassium nitrate of commerce is made from the cheaper salt, sodium nitrate, by acting upon it with potassium chloride. At low temperatures potassium nitrate is much less soluble than any of the other three salts present. From the equation—



it will be seen that there are present the nitrates of sodium and potassium and the chlorides of the same metals. On examination of the solubility curves of these salts (fig. 63) it will be noticed that, on evaporating a solution containing all four, the first salt to separate will be sodium chloride, and on further concentration potassium nitrate will crystallize out.

Solutions manifest many peculiar properties, and these will be considered when we have discussed the theory that has been put forward to account for the various phenomena observed in this connection. It may also be remarked in passing that the theory of solutions seems likely to profoundly modify our ideas regarding the genesis of igneous rocks.

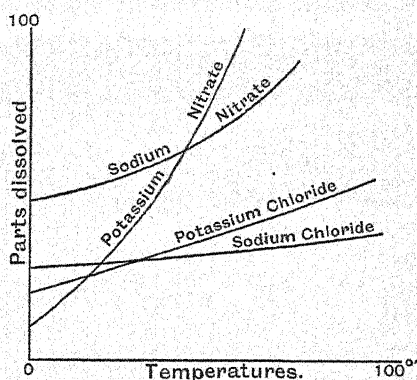


Fig. 63.—Curve showing Solubilities of Different Salts

### OSMOTIC PRESSURE

If a solution of a substance be placed in a vessel, and then the pure solvent carefully introduced so that the lower layer remains undisturbed, it will be found after a time that what was pure solvent is now solution: in other words, that diffusion of the two liquids has taken place. It may be supposed that some force is present which drives the dissolved substance from a region of greater concentration to one of lower. To this force the name of **OSMOTIC PRESSURE** has been given.

**NOLLET'S EXPERIMENTS.**—About the middle of the eighteenth century the Abbé Nollet demonstrated the existence of this force by taking a glass

tube containing alcohol, and closed at one end with parchment; and then immersing it in water. Water passed into the tube, but the alcohol could not escape through the parchment, consequently the level of the liquid in the tube rose, showing clearly that a definite pressure did exist.

**TRAUBE'S ARTIFICIAL MEMBRANES.**—In 1867 Traube showed that osmotic pressure could be demonstrated by using instead of an animal membrane such as parchment a thin film of a chemical substance. This he called a semi-permeable membrane, since it allows of the passage of solvent but not of the dissolved substance.

**WORK OF PFEFFER.**—In 1877 Pfeffer was successful in preparing semi-permeable membranes of such efficiency that he was able to measure the osmotic pressure of many solutions. The method adopted was as follows.

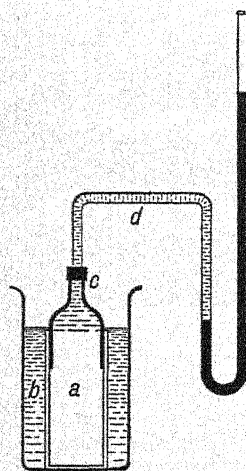


Fig. 64.—Cell with Semi-permeable Membrane connected with Manometer

Unglazed porcelain cells, such as are used in electrical batteries, were thoroughly saturated with water, care being taken first to remove all air by means of the air pump. They were then filled with a solution (3 per cent) of copper sulphate, and at the same time immersed in a similar solution. After standing thus for some hours, the solution inside the cell was poured out and the interior well rinsed with water, then dried as quickly as possible with strips of filter paper. A 3-per-cent solution of potassium ferrocyanide was then poured into the cell, which was again at once replaced in the copper sulphate.

When the cell had stood for about two days it was again filled with the potassium ferrocyanide solution, and then connected with a manometer, as shown in the accompanying figure (fig. 64). A rise in pressure was observed, due to the fact that the solution in the cell had a greater osmotic pressure than the copper sulphate which surrounded the cell.

The semi-permeable membrane is of course formed within the wall of the cell at the point where the two solutions meet. At this point insoluble copper ferrocyanide is precipitated, and this allows water but not salts to pass through, so that the volume within the cell must increase, and a measure of this can be obtained by noting the difference in the level of the mercury in the two limbs of the manometer.

Other methods have been devised for the purpose of determining osmotic pressures, of which brief mention may be made.



METHOD OF DE VRIES.—The method adopted by de Vries was to take certain plant cells, such as those found in the leaves of *Tradescantia discolor* and in *Curcuma rubricaulis*, and to place them in solutions of which it was desired to measure the osmotic pressure. If the solution in which the cells are placed has a greater osmotic pressure than the protoplasmic contents of the cell, then water will pass out from the cell and the contents will shrink away from the walls and tend to collect in the centre of the cell. If, on the other hand, the external solution has a lower osmotic pressure than the cell contents, then water will pass into the cell and the walls will be distended. Using this method, de Vries was able to prepare solutions which had the same osmotic pressure. Such solutions are said to be ISOTONIC.

METHOD OF DONDEERS AND HAMBURGER.—Another ingenious method, due to Donders and Hamburger, consisted in the employment of the red blood corpuscles of the deer and frog. The blood was first defibrinated (*i.e.* whipped with twigs to prevent clotting), and it was then found that if a solution of potassium nitrate (1.04 per cent) was added, the red corpuscles settled to the bottom of the vessel, leaving a clear solution. If the solution added was less than 0.96 per cent in strength the corpuscles did not settle completely, and two layers were present, the upper one being more or less coloured, according as the solution added differed widely or little from the standard strength mentioned above.

METHOD OF WLADIMIROFF.—Yet one further method is of interest, that of Wladimiroff. This observer found that the movements of certain bacteria were affected by the strength of salt solutions. As the solutions became more concentrated the movements grew slower, and by taking different salts it was possible to prepare isotonic solutions.

MEANING OF OSMOTIC PRESSURE.—The explanations of the phenomenon of osmotic pressure are not by any means satisfactory. At first sight it might be thought that the membrane allows the molecules of water to pass but not those of the substance dissolved. If, however, a mixture of propyl alcohol and water be placed in a semi-permeable cell, and surrounded with water, the water passes into the cell and no alcohol escapes. If, on the other hand, the cell is placed in propyl alcohol, it is the alcohol that enters. It would seem, therefore, that the membrane permits either water or alcohol to pass but is impermeable to a mixture of the two.

Another possible explanation is that loose chemical compounds are formed on the surface of the membrane, and as the latter becomes satu-

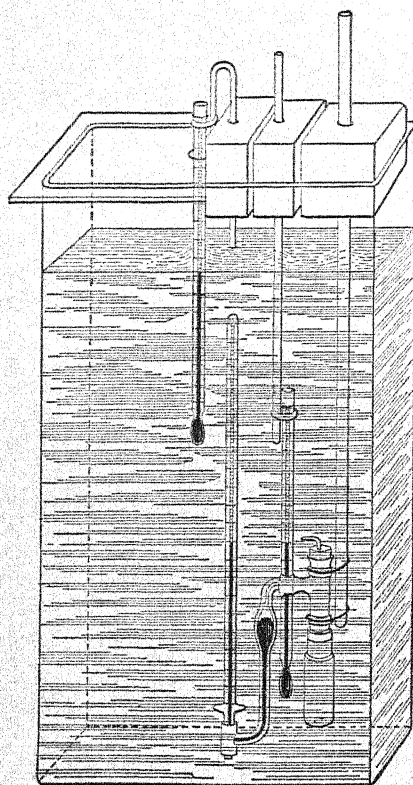


Fig. 65.—Apparatus for Measuring Osmotic Pressure

rated they break down on the side where the concentration is less.

But whatever be the real explanation of this phenomenon, certain facts of the highest importance have been observed, and some of these will be now considered.

The most accurate measurements of osmotic pressure were made by Pfeffer, who used the method described above. Great precautions were taken to ensure that the semi-permeable membrane was as perfect as possible, and the whole apparatus, including the manometer, was immersed in a bath which could be kept at a constant temperature (see fig. 65).

The first results to be considered are those in which the effect of change in concentration and temperature is seen. In the following table are measurements of the osmotic pressure of solutions of cane

sugar of different concentrations:—

C = Concentration in parts by weight in 100 parts of water.	P = Osmotic Pressure.	$\frac{P}{C}$
1	535 mm. of mercury.	535
2	1016 " "	508
4	2082 " "	520
6	3075 " "	512

The effect of change in temperature is clearly seen on examination of the following results obtained by Pfeffer:—

Temperature.	Osmotic Pressure.
6.8° ... ..	505 mm. of mercury.
13.2° ... ..	521 " "
14.2° ... ..	531 " "
22.0° ... ..	548 " "
36.0° ... ..	567 " "



Boyle's Law states that the pressure of a gas varies directly as the concentration, and Gay-Lussac's Law that the pressure increases with rise of temperature at the rate of one two-hundred-and-seventy-third for every degree Centigrade. Pfeffer's results show that the osmotic pressure of a solution obeys the same two laws, so that we cannot help noticing the close similarity existing between a gas and a solution.

This similarity is still more strikingly manifested when we compare the osmotic pressure of a solution of cane sugar and the gas pressure of hydrogen under the same conditions.

Pfeffer found that at  $6.8^{\circ}$  a 1-per-cent solution of sugar gave an osmotic pressure of 505 mm. of mercury. Cane sugar has a molecular weight of 342, corresponding to the formula  $C_{12}H_{22}O_{11}$ , so that a 1-per-cent solution contains  $\frac{10}{342}$  of a gramme-molecule in one litre. A volume of hydrogen which contained  $\frac{10}{342}$  of a gramme-molecule in one litre would exert a pressure at  $6.8^{\circ}$  of—

$$\frac{10}{342} \times 22.32^* \times \frac{279.8}{273} \times 760 = 508 \text{ mm. of mercury.}$$

APPLICATION OF GAS LAWS.—We must therefore conclude that in solutions such as the one just considered, the three gas laws of Boyle, Gay-Lussac, and Avogadro hold as in the case of gases. They may be stated as follows:—

1. The osmotic pressure is proportional to the concentration, or inversely proportional to the volume occupied by a given mass.
2. The osmotic pressure is proportional to the absolute temperature, or, in other words, that for an increase of  $1^{\circ}$  C. the pressure increases by one two-hundred-and-seventy-third.
3. Solutions of the same osmotic pressure contain the same number of molecules in a given volume.
4. The osmotic pressure of a solution is the same as the pressure of a gas containing the same number of molecules in a given volume.

LAW OF BLAGDEN.—It has been shown theoretically that a connection exists between the osmotic pressure and the freezing-point of a solution, but long before this was established it was known that a solution freezes at a lower temperature than the pure solvent. As long ago as 1788 Blagden showed that the lowering of the freezing-point was pro-

\* 22.32 is the volume occupied by a gramme-molecule (that is the molecular weight expressed in grammes) of any gas at normal temperature and pressure.  $\frac{279.8}{273}$  represents the increase in pressure due to a rise of  $6.8^{\circ}$  above the normal.

portional to the amount of the substance dissolved. This law of Blagden is, however, only an approximation, and more recent work has shown that the lowering becomes proportionally less as the concentration increases.

**WORK OF RAOULT.**—The foundations of our knowledge of this subject were laid by the French chemist Raoult, who conducted a large number

of experiments, using many solvents and different chemical compounds. Before describing the results which Raoult obtained, it will be necessary to give an account of the apparatus which is best adapted for measuring the lowering of the freezing-point. The one most used is that designed by Beckmann and shown in the accompanying figure.

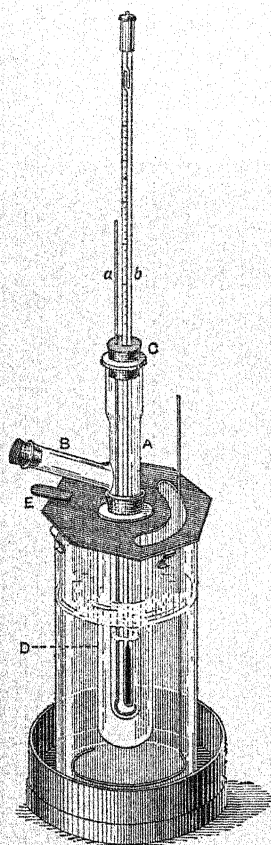


Fig. 66.—Beckmann's Apparatus for Measuring the Depression of the Freezing-point

The tube A, with its attached side tube, is placed inside a wider glass tube D, so that between the two there is an air space. A is tightly closed by a rubber stopper, through which passes a thermometer the construction of which will be described later, and a narrow glass tube which serves as a guide for a stirrer *a*, made either of glass or (preferably) of platinum. This part of the apparatus rests on a metal cover, which is placed on a stout glass jar E. The cover usually has two perforations, one for a thermometer and the other for a large stirrer. The liquid under investigation is placed in A, and a cooling mixture in the jar E. The air-space between A and D prevents the too-sudden cooling of the liquid in A.

The Beckmann differential thermometer is quite different from any other instrument in use. The bulb is very large, and the mercury thread very fine, so that a slight rise of temperature causes an appreciable difference in the height of the thread. But it is the upper end of the thermometer that calls for special comment. This, instead of terminating in the usual way, is expanded into a reservoir into which mercury may be driven by warming the bulb. It is thus possible to increase or decrease the amount of mercury in the bulb, so that the end of the mercury thread comes to any desired point on the scale. By warming the bulb, and then gently tapping the reservoir, some of the mercury will be detached, and on



again cooling the thread comes to a lower point on the scale. This is done when it is desired to measure comparatively high temperatures. If, on the other hand, the solution has a low freezing-point, the thermometer is inverted and the bulb cooled, and more mercury allowed to pass into the bulb. Since the operation in question is the measurement of differences of temperature only, it is not necessary to know the precise value of the fixed points on the scale, the one important thing being that the divisions on the thermometer should all be equal. Such a thermometer as the one described is usually graduated in hundredths of a degree, so that with a lens it is possible to read to a thousandth part of a degree.

The manner of carrying out a determination of this kind is briefly as follows: The solvent is placed in the carefully dried and weighed tube A, and then the whole again weighed. It is then introduced into the air jacket, and the whole then placed in the cooling mixture in the jar. The temperature of this is so adjusted that it remains only a degree or two below the freezing-point of the solvent. The temperature of the solvent gradually falls until it is about one-fifth of a degree below the true freezing-point. With the aid of the stirrer  $\alpha$  it is then thoroughly well agitated, and minute crystals of the solid appear, and at the same time the mercury rises rapidly, and finally becomes stationary at a point which is regarded as the true freezing-point of the solvent. The tube is then taken out of the cooling mixture and the crystals allowed to melt. The freezing-point is again determined with the same quantity of solvent, and the two determinations should be found to differ by only one-hundredth or so of a degree.

Through the side tube B a weighed amount of the substance is introduced, and the same procedure for determining the freezing-point followed. Two or three readings ought always to be taken, and these should correspond quite closely. The difference between the freezing-point of the pure solvent and that of the solution is known as the "lowering".

**RAOULT'S RESULTS.**—Some striking results were obtained by Raoult, the most important of which is the following: If in a solution containing 1 gm. of substance in 100 gm. of the solvent a lowering of  $L$  is produced, then the product of this quantity and the molecular weight of the substance is a constant for the particular solvent. This lowering is called the **MOLECULAR LOWERING**, and it is easy to see that if the constant is known it is possible to determine the molecular weight of any given substance which is soluble in that solvent.

The constants for certain solvents have been frequently determined and found to be as follows:—

Acetic acid...	...	...	...	...	...	39
Benzene ...	...	...	...	...	...	50
Formic acid	...	...	...	...	...	28
Nitrobenzene	...	...	...	...	...	71
Water ...	...	...	...	...	...	19

Similar results have been obtained in the case of metals. Heycock and Neville, for example, found that most metals, when dissolved in molten tin, produced a molecular lowering of about 3.

Another method which has been of service in determining molecular weights depends upon the fact that the vapour pressure of a solution is less than that of the pure solvent, and this difference can be most easily measured by observing the rise in boiling-point, since, if the vapour pressure is less, the solution will boil at a higher temperature. Various forms of apparatus for the purpose of measuring these differences have been devised, and this method, together with the one just described, have placed in the hands of the chemist valuable means of determining that important quantity, the molecular weight.

On examination of a large number of results, obtained by both the methods above described, it is found that in the case of certain substances, more particularly metallic salts in aqueous solution, abnormal values occur. With the object of explaining these and other facts that have been observed, a theory of solution has been put forward, the bearing of which upon chemical thought has been so important that an account of it must be given.

#### THE ELECTROLYTIC THEORY OF SOLUTION

**ELECTROLYSIS—THEORY OF GROTHUSS.**—Early in the nineteenth century Faraday began his work on the decomposition of chemical compounds by the electric current. This process was termed by him **ELECTROLYSIS**. Amongst the many theories propounded to account for electrolysis the first that was at all satisfactory was that of Grotthuss. Dealing with the decomposition of water, he said that when the elements hydrogen and oxygen separate from one another, the former becomes positively charged, and is attracted to the negative pole, while the latter has the opposite charge, and so is attracted to the positive pole.

**THEORY OF CLAUSIUS.**—According to this view, before an atom of hydrogen can be set free the current must be sufficiently strong to decom-



pose a molecule of water. Clausius showed that this theory was untenable, and, since the weakest current could cause the electrolysis of water containing a little acid, suggested that before the current passed there was a partial breaking down of the molecules. The effect of the current therefore was merely to exercise a directive action upon the parts into which the molecule had broken down. This idea has been most fruitful in results, and the theory of electrolytic dissociation, as it is called, is to-day almost universally accepted by the scientific world.

**IONS.**—Let us take, for example, a solution of common salt in water. If we accept the above theory we must regard this solution as containing not only molecules of sodium chloride, but also particles of sodium and of chlorine. These particles present in solution are called **IONS**, and to them are assigned special properties which we must now consider. It may be asked why, if a particle of sodium is present in water, does it not decompose the water with the evolution of hydrogen and the formation of caustic soda? The answer given to this question is that the ion of sodium and of every other element is not identical with the atom, but differs from it in that it possesses an electric charge. On passing an electric current through such a solution, the ion is led either to the positive pole or anode, or to the negative pole or cathode, and there gives up its charge, at the same time being changed into the atomic state.

If this be so, then the ions must move with certain velocities, and attempts have been made successfully to measure the rates at which ions move.

**VELOCITY OF IONS—WORK OF OSTWALD.**—If a current is passed through a solution of copper sulphate (the electrodes used being of copper), there will be a deposition of that metal at the cathode, and the same amount will be dissolved from the anode. Thus the total quantity of copper in the solution will remain unchanged. But it is found in such a case that the colour round the anode is deeper than round the other electrode. To explain this it was suggested by Hittorf that the ions moved with varying velocities, that is to say, either the **ANION** (*i.e.* the ion which separates at the anode) or the **CATION** (the one which separates at the cathode) had the greater velocity. In a remarkably clear way Ostwald showed how this explanation accounts for facts like the one mentioned above. In the following diagrams (fig. 67) the plain circles represent anions, and those with a cross the cations. It will be noticed that there is an equal number of each on either side of the median line before electrolysis begins.

Suppose that the velocity of the anion is twice that of the cation.

Then after three molecules have been electrolyzed the state of things seen in B will exist. Three anions and three cations will have been set free, but the undecomposed substance is more concentrated on the anode side of the median line, and after the ions have been liberated C represents the condition. Various methods have been devised for measuring the velocities, both relative and absolute, of the ions, but the details are too complicated to be given.

**THEORY OF ELECTROLYTIC DISSOCIATION.**—In treating of the phenomena of osmotic pressure and the lowering of the freezing-point

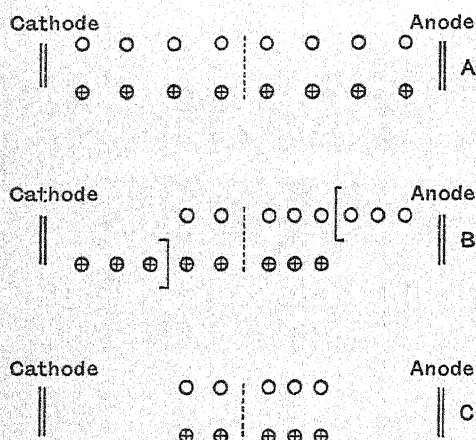


Fig. 67.—Diagram to illustrate the Migration of Ions

of solutions it was stated that abnormal results had been obtained. These can be well explained by the theory of ELECTROLYTIC DISSOCIATION originally propounded by Clausius and since developed by Arrhenius. It was mentioned that there were close analogies existing between the osmotic pressure of a solution and the pressure of a gas, and it was further stated that the osmotic pressure must be regarded as being due to the

pressure exerted by the particles of the dissolved substance. It is clear, therefore, that if the number of particles is increased then the pressure is likewise increased, and since the lowering of the freezing-point is intimately connected with the osmotic pressure, this will also be increased.

**ELECTROLYTES.**—It is found that all substances which allow of the passage of the electric current give abnormal values when either the osmotic pressure or any of the values depending upon it are determined. Consequently we are forced to the view that in dilute solution all those substances which conduct the electric current—ELECTROLYTES, as they are called—are dissociated into their constituent ions. On the other hand, a compound such as cane sugar is not dissociated, and, in consequence, the values obtained are normal.

**APPLICATIONS OF THE IONIC THEORY.**—The applications of this theory are wide and far-reaching, and by means of it many facts which had hitherto remained unexplained have become intelligible. For example, if a solution of silver nitrate be added to one of sodium chloride, a white



precipitate of insoluble silver chloride is produced. If, however, chloroform be substituted for the sodium chloride, no precipitate is obtained. The difference between the two cases is this: Sodium chloride is an electrolyte, and is therefore dissociated into its ions. Similarly the silver nitrate is dissociated, and the ions of silver and chlorine combine to form insoluble silver chloride. In the case where chloroform is used there is no dissociation into chlorine ions, and therefore no reaction between silver and chlorine can take place. We can lay down a new rule concerning the occurrence of chemical reactions, to the effect that reactions of the above nature take place between ions, and if these are not present then reactions either do not occur or, if they do, a considerable period of time is necessary for their completion.

Broadly speaking, salts, strong mineral acids, and bases are electrolytes, while neutral organic compounds, such as hydrocarbons, alcohols, ethers, &c., are non-electrolytes.

Some interesting results connected with the properties of ions have been obtained, and a few of these may be mentioned.

**CHANGE OF COLOUR.**—It is a well-known fact that a solution of litmus is coloured red by acids and blue by alkalis. The most satisfactory explanation of this is found in the application of the electrolytic theory in the following way. Litmus is a weak acid, of which the molecules are red. In presence of a strong acid, that is to say, in the presence of an excess of hydrogen ions, into which all acids dissociate, it remains undissociated. This is accounted for by the statement, based upon many observations, that the presence of a common ion (in this case hydrogen ion) diminishes the dissociation. On the addition of an alkali a salt is formed, and this, like all salts, dissociates into a cation, say sodium ion or potassium ion, and the litmus anion. This anion is coloured blue, so that, as the sodium or potassium ion is colourless, the change of colour must be due to the appearance of the litmus anion.

Another illustration of the change of colour following upon the appearance of a new ion is one met with in the course of ordinary qualitative analysis. If to the deep-blue ammoniacal solution of copper sulphate a solution of potassium cyanide be added, the colour vanishes. Further, if through this solution a stream of sulphuretted hydrogen be passed, no precipitation of copper sulphide occurs. A new ion has been formed, and the cation is no longer copper but potassium, while the copper is combined with a cyanide group, forming a colourless anion. This complex ion is not decomposed by the sulphuretted hydrogen, and, as there are present no copper ions, no precipitation can take place.

The solution of potassium permanganate is of a deep-purple colour, and so are the solutions of all the soluble permanganates. If these solutions are examined in the spectroscope it is found that all give five absorption bands in the yellow and green portion of the spectrum. Ostwald carefully measured the position of these bands in a large number of permanganates in which the cation was colourless, and found that the positions of the bands was in all cases identical. This supports the view that in each case the salt had dissociated into its ions, and that the colour was due to the permanganate ion alone and not to the salt as a whole.

It may be mentioned that, in addition to the above, there are so-called chemical theories of solution which seek to explain facts by assuming the formation of definite chemical compounds between solvent and solute. Doubtless in many cases such compounds do exist, but the theory above described in brief outline has been of so much greater service in accounting for observed facts that at present it is the one mainly supported. It serves to explain phenomena which the chemical theory cannot illuminate, and it further suggests new lines for future work, thereby fulfilling in the highest degree the functions of a theory.

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## CHAPTER V

### THE CHEMISTRY OF LIFE

The animal body is made up of a series of complex compounds, of which the main constituents are carbon, hydrogen, nitrogen, oxygen, sulphur, and phosphorus. In addition to these there are certain mineral constituents present for the most part in the bones and hard tissues.

The vital functions are maintained by means of the energy derived from the breaking down of the tissues, and, in order to make good the loss, new supplies of foodstuffs, from which new tissues can be formed, must be provided.

In the following pages a short account of the composition of the various foodstuffs will be given, and at the same time an attempt will be made to trace the fate of these substances, showing how by chemical processes they are transformed so as to be capable of assimilation by the body.

In addition to the inorganic salts, which are necessary for the proper maintenance of the economy, foodstuffs may be divided into three main



classes, namely, carbohydrates, fats, and proteids. Each of these has its own special work to do in the animal organism, and for an account of this reference must be made to the section dealing with physiology. Here we are concerned with the chemical aspect of the problem.

**CARBOHYDRATES.**—The term carbohydrates includes compounds which are made up of carbon, hydrogen, and oxygen. The name was originally given to them because the members of the series first known contained the elements hydrogen and oxygen in the proportions in which they occur in water. The name has become a general one, and now includes a variety of products in some of which the proportion above mentioned does not hold. They are usually divided into three classes, according to the degree of complexity which they exhibit.

1. **MONOSES.**—The monoses are the simplest members of the carbohydrate group. They are all alcohols, containing either an aldehyde or a ketone group. The simplest monose is **GLYCOLLIC ALDEHYDE**, which has the structure—



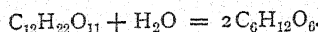
The most complex is a synthetic sugar prepared by Fischer, containing nine carbon atoms. Between these two extremes are many compounds, some of which occur naturally, while others have been obtained by synthetic methods.

A few sugars containing five carbon atoms, such as **ARABINOSE** and **XYLOSE**, are readily formed from natural products, the former from cherry gum and the latter from wood gum, straw, and jute, by boiling with dilute sulphuric acid. The majority of the naturally occurring monoses are, however, hexoses, that is to say, compounds containing six carbon atoms. Included among the hexoses are **GLUCOSE** or grape sugar, **FRUCTOSE** or fruit sugar, and **GALACTOSE**, a substance obtainable from milk sugar. Reference has already been made to these compounds when discussing stereoisomerism, and it will suffice here merely to state that they are represented by the formula—

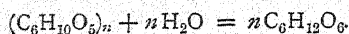


2. **BIOSSES AND TRIOSSES.**—These compounds may be regarded as derived from the monoses by condensation of two or three molecules with the elimination of either one or two molecules of water. In this sense they are the anhydrides of the monoses. Amongst them we must mention **CANE SUGAR**, **MALT SUGAR**, and **MILK SUGAR**. On treatment with dilute acids or alkalis, or even on prolonged boiling with water, they are again

converted into the hexoses from which they are theoretically derived. Thus cane sugar on hydrolysis yields glucose and fructose, maltose (malt sugar) yields glucose only, while from lactose (milk sugar) glucose and galactose are obtained. These reactions can be represented by the equation—



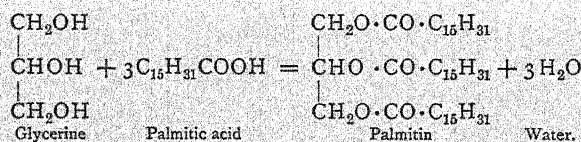
3. POLYPOSES.—This group includes a number of very complex compounds, the actual composition of which is in many cases unknown. Such substances are STARCH, CELLULOSE, and various products obtained from them. They can all be represented by the formula  $(C_6H_{10}O_5)_n$ , and by addition of water it will be seen that they readily pass into monoses.



As a general rule the form in which carbohydrates occur in food is that of a biose or a polyose. The most frequently occurring are cane sugar and starch, of which the former is soluble while the latter is not. Apparently the only form in which carbohydrates are assimilated by the body is glucose (or in some cases fructose). Consequently, before any starch can be of service it must be broken down by a process of hydrolysis. This, as we have seen, can be performed by dilute acids, but in the body the change is effected by a FERMENT. The saliva contains such a ferment, known as PTYALIN, which in an alkaline medium is able to convert starch into sugar. In the secretion of the pancreas there is also present a ferment, AMYLOPSIN, which has the same effect, and by means of these two ferments most of the carbohydrate part of the food is transformed into a form in which it can be absorbed and stored until such time as it is required to provide energy for the organism. It may be mentioned that the glucose absorbed from the intestines is stored in the liver as GLYCOGEN or animal starch. This substance is readily retransformed into glucose.

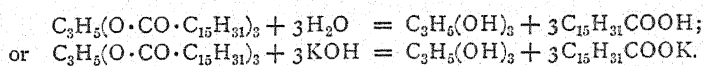
(For other ferments or enzymes which act upon carbohydrates see PHYSIOLOGY.)

FATS.—Most animal fats consist mainly of compounds of the higher fatty acids with glycerine. These compounds are ESTERS, the three most common being PALMITIN, STEARIN, and OLEIN. Such a fat is formed by the condensation of one molecule of glycerine with three molecules of the acid according to the following equation:—





Olein is a liquid, stearin and palmitin are solids, so that the consistency of a fat depends upon the proportion in which these three esters occur. All fats can be saponified or hydrolyzed by boiling with dilute alkalis or by treatment with superheated steam, the process consisting simply in the addition of water, whereby free glycerine and the fatty acid or its alkali salt are formed. Thus palmitin gives glycerine and palmitic acid or potassium palmitate—



In the body a similar change is effected by a ferment present in the pancreatic secretion which splits up the fat into its constituents. These are absorbed from the intestine and are again built up into the fatty part of the tissues.

PROTEIDS.—Under this heading is included a large number of exceedingly complex compounds, which as a general rule are composed of hydrogen, oxygen, carbon, nitrogen, and sulphur. The percentage composition of the various proteids differs but little. They contain—

$$\begin{aligned} \text{C} &= 52.7 \text{ to } 54.5 \% & \text{H} &= 6.9 \text{ to } 7.3 \% & \text{N} &= 15.4 \text{ to } 16.5 \% & \text{O} &= 20.9 \text{ to } 23.5 \% \\ & & \text{S} &= 0.8 \text{ to } 2.0 \%. \end{aligned}$$

So little is known of the chemical nature of these substances that at present nothing more than a rough classification is possible. One of the most satisfactory of the proposed classifications is the following:—

1. SIMPLE ALBUMINS.—This group includes compounds like egg albumin, found in the white of birds' eggs; serum albumin, present in all tissue fluids; myosin from muscle; globulins, and other substances, such as casein.

2. PROTEOSES.—These are the decomposition products of the simple albumins and are formed either by the action of acids and alkalis or by the action of the natural ferments occurring in the animal.

3. COMPOUND ALBUMINS.—To these compounds it has been proposed to restrict the name proteid. Included in this class are substances found in cell nuclei. They are interesting to the chemist, since on hydrolysis they break down into albumins and derivatives of nucleic acids, which latter are allied to a group of compounds the constitution of which is well known, namely the purine group. Also belonging to this group are substances like hæmoglobin, the colouring matter of blood, and allied substances.

4. ALBUMINOIDS.—This term is applied to a variety of complex com-

pounds which form part of the animal tissues, such as keratin, found in the hair and nails; elastin, in the ligaments; and substances obtained from cartilage.

Many attempts have been made to ascertain the nature of this obscure group of compounds both by analytical and synthetical methods. A great number of decomposition products have been obtained as the result of the hydrolytic breakdown of the proteid complex, and amongst these the following classes of compounds are worthy of mention:—

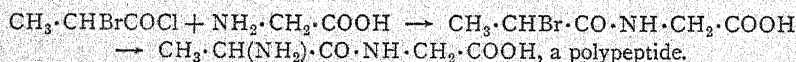
1. AMIDO COMPOUNDS, including ammonia, urea, and the amino-acids.

2. HETEROCYCLIC COMPOUNDS, that is to say, compounds of which the structure is best represented by a closed ring made up of carbon and other atoms (chiefly nitrogen).

3. CARBOHYDRATES.—The hydrolysis of proteids is usually carried out by boiling with either baryta water or with an acid. If hydrochloric acid is employed, use is made of the concentrated solution; but if the acid chosen is sulphuric, then it is generally much diluted.

EMIL FISCHER'S WORK.—For the separation of the products of hydrolysis a convenient method has been worked out by Emil Fischer. He converts the acids formed into esters by treating the solution with a 3-per-cent alcoholic solution of hydrochloric acid, and then fractionally distills the mixture under reduced pressure. In this way he has succeeded in isolating a number of products the existence of which was previously unsuspected.

To the same worker are due attempts to synthesize substances of a proteid-like nature. By condensing the halogen derivative of a fatty acid chloride with an amino acid, and then replacing the halogen by the amino group, Fischer has succeeded in preparing compounds to which he has given the name POLYPEPTIDES. A simple polypeptide is formed in the following manner:—

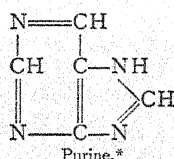


In many respects these compounds closely resemble various bodies derived from proteids as a result of digestion within the body, and though no claim is made that proteids have actually been synthesized, yet it seems that we are a step nearer to the understanding of the nature of this baffling group.

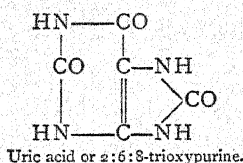
During digestion a variety of products is formed as the result of the action of the ferments contained in the secretions of the gastric glands



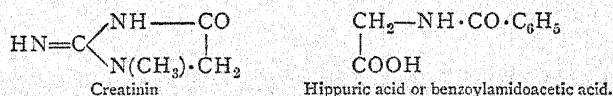
and the pancreas. It seems that the proteid is broken down successively into bodies of increasing simplicity until peptones are obtained. These are absorbed by the blood and are then built up into the body tissues. As a result of activity the tissues are broken down to provide energy, and comparatively simple compounds are formed. These may be supposed to contain no further available energy, and in consequence are excreted. Amongst such excretory products are urea and substances known as the purine bases. These latter are derived from PURINE, which has the composition represented by the formula—



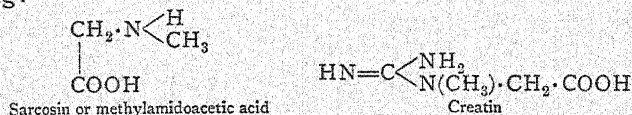
Uric acid is the main form in which nitrogenous waste is excreted in reptiles and birds, but it is also present in small quantities in the urine of the mammalia. It is a trihydroxy derivative of purine, and has the formula—



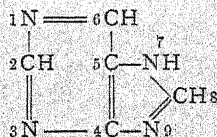
The other nitrogenous compounds present in urine are creatinin and hippuric acid, together with small amounts of ammonia.



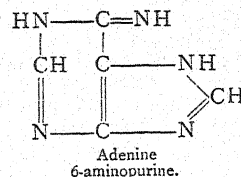
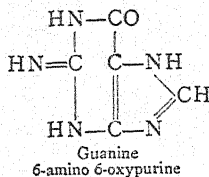
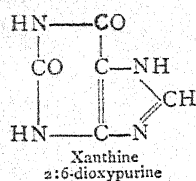
Amongst other nitrogen derivatives found in the animal body are the following:—



\* For purposes of nomenclature the atoms are numbered thus:—



and the following purine derivatives—



### NUTRITION OF PLANTS

The nutrition of plants is different from that of animals in this respect. Whereas animals can only build up their tissues at the expense of complicated compounds like carbohydrates and proteids, green plants, by the aid of sunlight and moisture, convert the carbon dioxide of the atmosphere into carbohydrates, which, with the nitrogenous constituents present in the soil, suffice for their needs.

It has been suggested by Baeyer that the carbon dioxide is first reduced to formaldehyde,  $\text{CH}_2\text{O}$ , which is then condensed to a monose according to the following equation:—



The monose thus produced is then converted into the polyose, starch.

A certain amount of colour is lent to this hypothesis by the fact that it is possible to convert a solution of formaldehyde into a sweet syrupy substance having the formula—



As to the manner in which the complex framework of the plant is formed nothing is known. This consists mainly of cellulose, another polyose of unknown constitution.

**RESINS AND CAOUTCHOUC.**—In addition to these compounds there are many products synthesized by the plant which are of considerable interest. Amongst these may be mentioned resins and substances like caoutchouc. The latter is found as a milky juice in certain plants, such as those belonging to the genera *Siphonia* and *Ficus*. On exposure to the air it is converted into the familiar **INDIARUBBER**. This, when treated with compounds containing sulphur, is hardened, and is then known as **VULCANITE**.

**ESSENTIAL OILS.**—Many plants contain essential oils, which are complex mixtures of alcohols, esters, and hydrocarbons belonging to a series called the **TERPENES**. Such oils are those of lavender, rosemary, thyme, &c. A familiar instance of an essential oil is that of turpentine, obtained



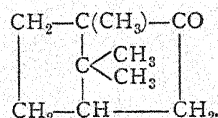
from various kinds of pine trees. The main constituent of this oil is a hydrocarbon PINENE, a substance which can exist in two optically active forms. The pinene from American turpentine is dextrorotatory, while that from French oil is lævorotatory.

Of other hydrocarbons belonging to this series must be mentioned LIMONENE, found in oil of citron, oil of bergamot, and in the oil obtained from orange rind.

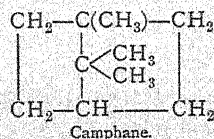
The alcohols most commonly present in the essential oils are GERANIOL, found in oil of rose and oil of geranium; LINALOOL, found in considerable quantities in oil of lavender; MENTHOL, the constituent to which oil of peppermint owes its characteristic smell; and BORNEOL, found in Borneo camphor, which on oxidation yields camphor.

Perhaps the most important member of this group is CAMPHOR, which is obtained from the camphor tree (*Laurus Camphora*). It is obtained by distillation of the wood of the latter in steam.

CAMPBOR.—There are few naturally occurring compounds to which so much attention has been paid as camphor. The problem of the constitution of this substance has engaged the notice of many chemists, and only comparatively recently has it been definitely settled. Because of the ease with which camphor can be transformed into benzene derivatives, Kekulé suggested that it was a simple ring compound; but as such a constitution failed to explain its behaviour, a number of other formulæ were proposed. In 1893 Bredt assigned the following as being the one which most adequately represented the reactions which camphor undergoes when treated with various reagents.

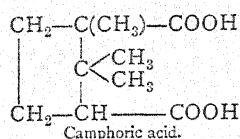


It will be seen that camphor is a ring compound, but not a simple one, as it contains another one within the main ring. Such a compound is known as having a *bridged-ring* structure. Camphor is therefore a ketonic compound, as it contains the carbonyl group,  $>\text{C}=\text{O}$ . It is derived from the hydrocarbon camphane, to which the constitution—



has been assigned. On oxidation with nitric acid camphor gives a diabasic

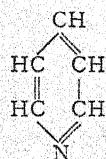
acid, camphoric acid, which, if camphor has the structure already given, must be represented by the formula—



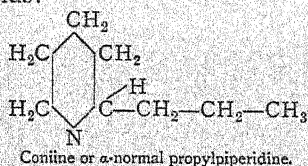
Confirmation of this has been provided by a recent synthesis of the acid by Komppa, from which there is little doubt that the constitution of the parent substance is accurately known.

**ALKALOIDS.**—Amongst the most important of plant products are the alkaloids. These are, generally speaking, complex compounds containing carbon, hydrogen, oxygen, and nitrogen. They usually occur combined with some organic acid, such as malic or citric, and may be extracted from the plant by treatment with dilute acid. The acid solution is then neutralized with ammonia, and the free base extracted with chloroform. They are all basic, have usually a bitter taste, and are optically active. In many cases the constitution is unknown; in others it is known from what classes of compounds they are derived; and in a few cases the actual structure is definitely settled,

One of the simplest alkaloids is **CONIINE**, which is found in the hemlock (*Conium maculatum*). This substance is a derivative of pyridine, a compound to which the following constitutional formula is given:—

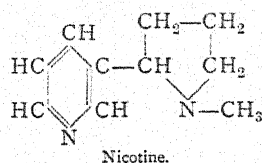


Ladenburg synthesized the alkaloid from pyridine, and obtained a product identical in all respects with the natural one, except that it was optically inactive. By the use of Pasteur's method he was able to resolve the inactive form into two optically active constituents, of which the dextro-compound was found to be absolutely identical with the coniine obtained from the hemlock plant. As a result of this synthesis, which is the first example of the artificial preparation of an alkaloid, we are able to write the formula of coniine thus:—





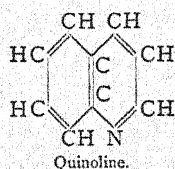
NICOTINE.—Another member of this group which has been synthetically prepared is nicotine. This synthesis was performed by Pictet, who showed that it was pyridyl-N-methyl pyrrolidine—



COCAINE, ATROPINE, AND ECGONINE.—An alkaloid at present much used in surgery is COCAINE, obtained from the coca leaf. It is closely allied to ATROPINE, found in the Deadly Nightshade (*Atropa Belladonna*) and to another alkaloid from the coca leaf called ECGONINE. The structure of these is known, but so far complete syntheses have not been carried out.

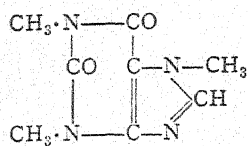
OPIUM.—From the dried juices of the white poppy (*Papaver somniferum*) OPIUM is obtained. This is a mixture of a large number of alkaloids, of which MORPHINE is the most important. The structure is unknown.

QUININE.—The alkaloids found in the barks of members of the *Cinchona* family, such as QUININE and CINCHONINE, are derivatives of QUINOLINE. This compound may be regarded as being a condensation product of benzene and pyridine, since synthesis has shown its structure to be—

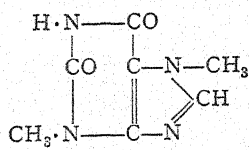


STRYCHNINE AND BRUCINE.—Also allied to the quinoline group of alkaloids are STRYCHNINE and BRUCINE, two exceedingly poisonous substances, which have so far resisted all attempts to ascertain their precise structure.

CAFFEINE AND THEOBROMINE.—Although not belonging to the group of alkaloids proper, mention may be made at this point of CAFFEINE and THEOBROMINE, obtained from coffee and cocoa respectively. The constitution of these has been established by Fischer, who showed that they were derived from purine, the parent substance of uric acid. Fischer succeeded in preparing them synthetically, and has shown that they are methyl derivatives of purine:—



Caffeine  
1:3:7-trimethyl-2:6-dioxypurine



Theobromine  
3:7-dimethyl-2:6-dioxypurine.

### DYESTUFFS

From an industrial point of view the natural dyestuffs are of the greatest importance, though with the extraordinary development of the coal-tar-colour industry this has somewhat diminished. Still at the present time the preparation of the dyestuffs and their application give employment to a large number of people.

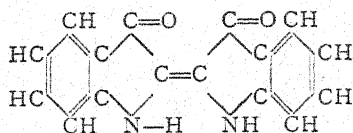
These substances, as will be seen, differ widely in composition, but of all of them it may be said that they are of a complicated nature. As a general rule they do not dye either animal or vegetable fibres directly, but require the assistance of a mordant.

**INDIGO.**—This, probably the most important of all the naturally occurring colouring matters, is found in the indigo plant (*Indigofera tinctoria*), and to a smaller extent in woad (*Isatis tinctoria*). It does not occur as such in the plant, but in the form of a glucoside, INDICAN. By the action of dilute acids or of air and water this is decomposed into indigotin and a sugar. The bulk of the colouring matter is present in the leaves, and these are cut off, collected, and taken to the factory, where they are placed in vats and steeped with water. By this means the glucoside is decomposed, and at the same time, probably as the result of the action of an enzyme present in the plant, the insoluble indigotin is converted into a soluble form, namely INDIGO WHITE. The solution is then vigorously stirred with paddles and so brought into contact with the air, and the indigo white is thereby converted into the insoluble indigo blue or INDIGOTIN, which is deposited at the bottom of the vat.

The constitution of indigo was established by Baeyer, who discovered several methods by which it could be artificially prepared. These methods were, however, not possible on a commercial scale for the manufacture of indigo, and other workers have since devoted their labours to the finding of a process which could be applied on a commercial basis. Such a process is the one devised by Heumann, and at present carried out by the *Badische Anilin und Soda Fabrik*. This synthetic method will be described later when dealing with the question of the coal-tar industry.

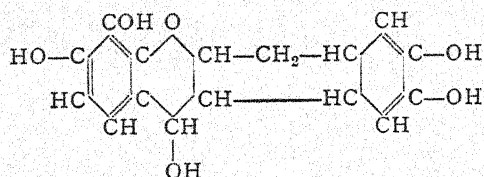


The constitutional formula of indigo is—

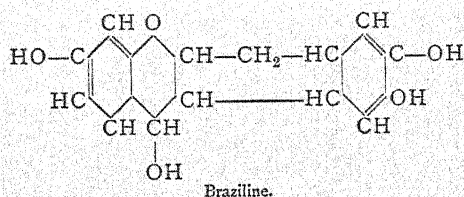


LOGWOOD.—This exceedingly important dyeing material is found in the wood of a tree (*Hæmatoxylon campechianum*) which grows chiefly in the West Indies and in Central America. For certain classes of goods, including silks and woollens, logwood is unsurpassed by any of the artificial dyestuffs. It is always used in conjunction with a mordant of iron or copper, with which it gives varying shades of black. The colours so obtained are characterized by the rich "bloom" which serves to make them held in high esteem.

A considerable amount of work has been done by W. H. Perkin, junior, and his pupils, on the constitution of hæmatoxylon, the active principle of logwood, and from the evidence so obtained the conclusion has been reached that this substance is best represented by the formula—



Of the natural products used in dyeing, mention must be made of the so-called redwoods. Under this name are included a variety of products such as Brazil wood and Lima wood. The active principle in all is a compound BRAZILINE, to which Perkin ascribes the formula—



There are many other natural products used in dyeing, but in almost all cases the constitution of the actual colouring matter is unknown. As examples of these may be mentioned the following: Turmeric, cutch or gambier, fustic, quercitron, archil, persio or cudbear, and saffron.

COCHINEAL.—The only dyestuff of animal origin that need be mentioned is COCHINEAL, formerly used for dyeing scarlets and crimsons. The

use of this substance has almost entirely been abandoned in favour of the synthetic products obtained from coal tar.

**TANNINS.**—In some plants there are found compounds known as tannins. These are of such a complex nature that their constitution is quite unknown. They seem to be compounds of acids, such as gallic and tannic acids, with various other substances. In some cases the acids are combined with sugars, since when the tannin is treated with dilute sulphuric acid sugar is formed.

## CHAPTER VI

### FUEL AND COAL-TAR INDUSTRY—EXPLOSIVES

#### FUEL

The fuels in general use are all derived from cellulose. When heated they combine with the oxygen of the atmosphere with the formation of carbon dioxide and water. The cellulose is synthesized from the carbon dioxide and water of the air by plants, and during combustion is reconverted into the same constituents.

**WOOD, PEAT, AND COAL.**—The substances most commonly used are the following, which are all cellulose in varying stages of decomposition. **COAL** is one of the last stages in the transformation of pure cellulose into a substance consisting practically of carbon. The accompanying table shows how the carbon continually increases, while the hydrogen and oxygen diminish in amount.

	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen and Nitrogen. Per cent.	Heat Value in Thermic Units.
Wood ...	49	6	45	4100
Peat ...	55	5	40	4500
Lignite ...	66	5	29	5700
Coal ...	86	4	10	8000
Anthracite	94	3	3	8200

**HEAT VALUE OF FUEL.**—This is of great importance from an industrial point of view, and can be determined either by analysis and subsequent calculation according to a formula, or more accurately by a direct determination of its calorific power. In this latter method a special form



of calorimeter is employed, for details of which a work on technological chemistry must be consulted.

In the above table it will be seen that ANTHRACITE, which of all forms of fuel contains the highest percentage of carbon, possesses the greatest calorific power. WOOD, on the other hand, consisting of practically pure cellulose, has less calorific power than any other fuel.

PEAT.—This is the decomposition product of plants, particularly marsh mosses, such as *Hypnum* and *Sphagnum*. The composition of peat differs according to the nature of the soil in which the plants grow, and upon the extent to which decomposition has proceeded.

As a fuel, peat has a low value, chiefly because the space occupied is great in proportion to the heat evolved. This defect is to some extent remedied by pressing the peat, but the added cost makes it still an expensive form of fuel, except for local use. Attempts have been made to obtain from peat various oils and other products by destructive distillation, but on account of the cheapness with which these can be obtained from other sources this industry is neither a large nor a flourishing one.

COAL.—The origin of coal is dealt with elsewhere. Here it must suffice to mention that the composition of coal varies according to its age, the conditions under which it was formed, and the nature of the plants from which it was formed.

The chief point in which one specimen is superior to another for heating purposes is the percentage amount of carbon. The greater the amount of carbon the greater, as a general rule, is the calorific power. This explains why the anthracite or steam coal of South Wales is so highly esteemed for industrial and naval work. It burns with a slightly luminous but smokeless flame, and it is this latter quality that renders it peculiarly valuable.

COKE—Coke is a product obtained from coal by a process of heating. This is conducted in such a way that the following objects are attained:—

1. The calorific power is increased, because the percentage of carbon is raised.
2. Evil-smelling constituents are expelled. (Important for household uses.)
3. There is less caking together. (Important for industrial uses, as in smelting, &c.)
4. A portion of the sulphur, always present as iron sulphide, is expelled.

Formerly coking was effected in much the same way as in the manufacture of charcoal. The coal was placed in heaps and burnt, with only a limited supply of air. The modern process, however, is conducted in

coking ovens, of which there are many types, the one most generally employed being that known as the Appolt oven.

In some cases a great feature is made of the recovery of the tar and ammonia, but as ovens of this type cost, to build, three or four times as much as the ordinary oven, the costliness is a great bar to their wider use, and it is only when the returns are exceedingly good that they can be profitably worked.

COALITE.—At the time of writing, a new product known as COALITE is being introduced to the public. The company responsible for its manufacture claim that its heating power is superior to that of coal, and approaches that of coke, while the disadvantages attending the use of the latter are absent. Further, they state that the by-products are such as will render profitable their working for benzene and like derivatives.

LIGNITE (BROWN COAL).—This may be regarded as a stage in the formation of coal intermediate between it and peat. Generally speaking, lignite requires much preparation before it can be used for ordinary heating purposes. For example, many specimens contain as much as 60 per cent moisture when freshly raised. Air drying reduces this amount to 15 or 20 per cent. In consequence many processes have been devised for remedying this defect, and these, together with a method by which the lignite is pressed to a more compact form, render the lignite more usable.

#### DESTRUCTIVE DISTILLATION

By the term destructive distillation is meant the decomposition of bodies by heat with recovery of the volatile products so formed. The substances usually subjected to this process are coal, wood, and certain other bodies of which mention will be made in the sequel.

The destructive distillation of coal is by far the most important of all, since the products thereby obtained are of immense value, and upon their recovery depends an enormous industry.

COAL TAR.—The coal tar obtained as a by-product in the manufacture of coal gas is the raw material from which a variety of products is prepared. A certain amount of tar is used as such for the preparation of lampblack, for the preservation of wood and ironwork, and for other purposes, but the main quantity is submitted to distillation for the recovery of substances such as benzene, naphthalene, phenol, anthracene, &c.

The process is usually carried out in stills of the kind shown in the accompanying figure (fig. 68).

DISTILLATION OF COAL TAR.—Such a still, constructed to receive a



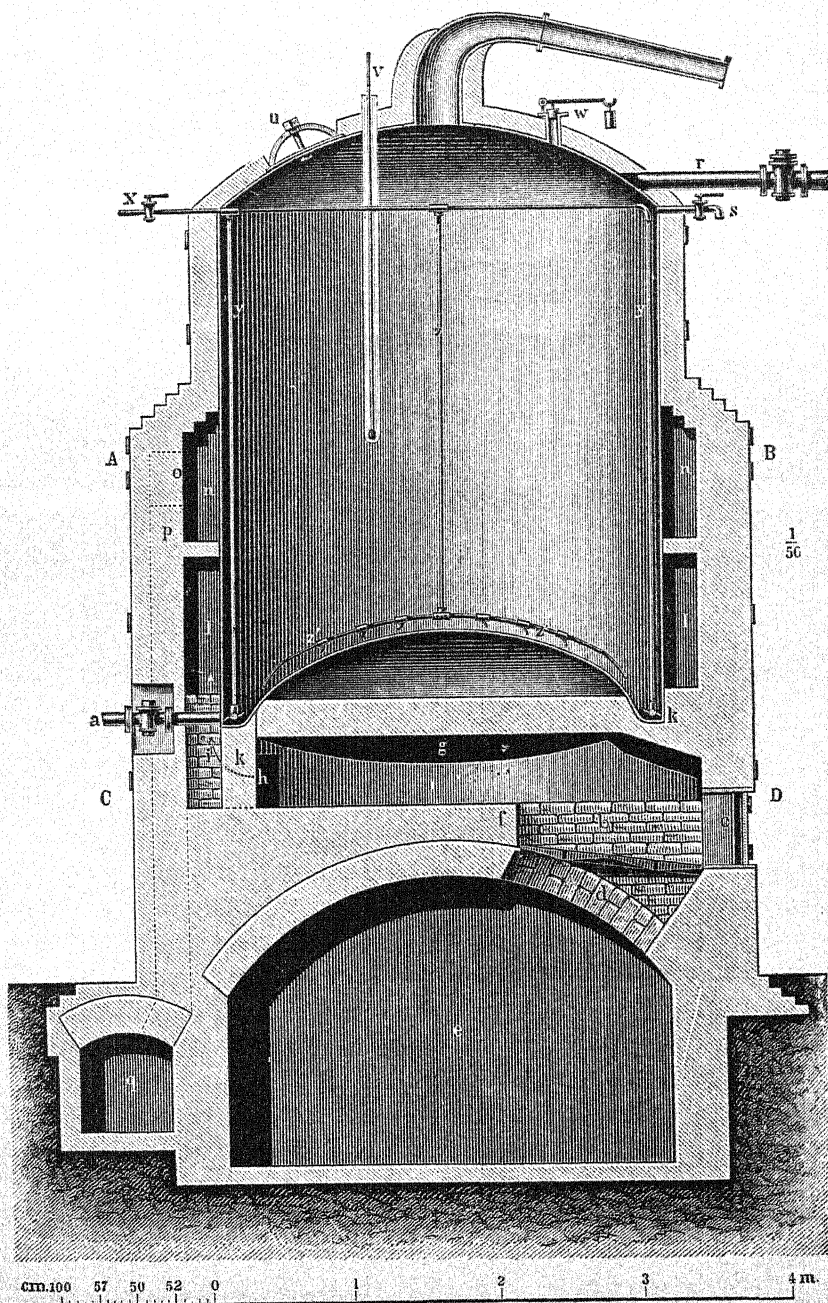


Fig. 68.—Coal-tar Still

charge of 25 tons of tar, is about 9 ft. 10 in. in width and 11 ft. 6 in. in height. It is made of boiler plates  $\frac{3}{8}$  to  $\frac{1}{2}$  in. in thickness. As will be seen from the figure, there is a concavity in the bottom which approximately corresponds to the concavity of the cover. An arrangement is provided by means of which steam can be blown through the still during the process of distillation.

The vapours are led away from the still into a cooler or condenser, made, like the still, of wrought iron. This is surrounded by water, but as the higher boiling fractions of the tar are solid at the ordinary temperature, it is necessary during the latest stages of the distillation to admit warm water or even steam, and an arrangement for this is also provided.

As long as any ammonia water is present there is a danger of the tar boiling over, so that at first the distillation must be conducted with caution. A thermometer is fixed in the still head, and according to its indications the following fractions are usually separated.

1. First runnings ...	...	...	...	...	up to 105° or 110°
2. Light oils ...	...	...	...	...	up to 210°
3. Carbolic oils (for phenol and naphthalene) ...	...	...	...	...	up to 240°
4. Heavy oils ...	...	...	...	...	up to 270°
5. Anthracene oils ...	...	...	...	...	above 270°

Each of these fractions is then worked up separately, and for this purpose stills of special construction are employed. The light oil, or crude naphtha as it is called sometimes, is treated with strong sulphuric acid and then with soda, to remove all resinous matter and other impurities, washed with water, and then re-distilled.

From this fraction are separated benzene (of different strengths, known as 90-per-cent, 50-per-cent, &c.), toluene, and xylene or xylol, the latter being a mixture of isomeric hydrocarbons.

The other fractions are similarly worked, and eventually a series of pure products is obtained.

The following table (taken from Lunge's *Coal Tar and Ammonia*) shows in a concise form the various products which are obtained from the different fractions.



## SYNOPSIS OF THE DISTILLATION OF COAL TAR

DEHYDRATION.—(a) By standing ... }  
 (b) During the heating up ... } AMMONIACAL LIQUOR.  
 DISTILLATION.—

I. *Fraction up to 170°* { ammoniacal liquor ...  
                                   *First runnings* rectified yield:—

1. Product up to 110°, chemically washed, distilled by steam, yields
  - (a) ... ..
  - (b) Weaker benzol goes to I, 2 ...
2. Product up to 140° treated like 1 yields (a) ... ..
- (b) ... .. 50 PER CENT BENZOL.
- (c) Intermediate fraction is redistilled.
- (d) ... ..
3. Product up to 170° treated like 1 and 2 yields (a) ... ..
- (b) ... .. SOLVENT NAPHTHA.
- (c) Residue goes to II. ... .. BURNING NAPHTHA.

II. *Fraction from 170°–230°. Middle oil* washed with caustic soda yields:—

1. Oil distilled in the light oil still; yields
  - (a) Distillate up to 170° goes to I, 3.
  - (b) Distillate up to 230° yields ... .. NAPHTHALENE.
  - (c) Residue goes to III.
2. Alkaline liquor decomposed by carbonic acid yields
  - (a) Aqueous solution of sodium carbonate, causticized by lime and used over again.
  - (b) Crude carbolic acid, which is purified and yields
    - (a) ... .. CARBOLIC ACID.
    - (β) Waste oils go back to II.

III. *Fraction from 230°–270°. Heavy oil* (collected till solid matters begin to crystallize) can be treated for naphthalene; usually only employed as ... .. CREOSOTE OIL.  
 Or else separated into (a) ... ..  
                                   (b) ... .. LUBRICATING OIL.

IV. *Fraction, Anthracene oil.* Filtered or cold-pressed, yields:—

1. Oils, are redistilled and yield
  - (a) Solid distillate, treated along with IV, 2.
  - (b) Liquid distillate goes to III, 6, or is redistilled.
  - (c) Residue (pitch, coke, &c.).

2. Residue is hot-pressed and yields
    - (a) Oils treated like IV, 1.
    - (b) Crude anthracene, washed with naphtha, &c., yields
      - (a) ... .. ANTHRACENE.
      - (b) Solution is distilled and yields
        - (aa) Naphtha, used over again for washing;
        - (bb) Phenanthrene, &c., is burnt to LAMPBLACK.
- V. *Pitch.* Employed for patent fuel or varnishes ... .. PITCH.
- Or else distilled, yielding :—
1. Crude anthracene, treated like IV, 2.
  2. Lubricating oil, goes to III, (a) and III, (b).
  3. Residue ... .. COKE.

### THE COAL-TAR INDUSTRY

The distillation of the crude coal tar, as just described, is only the first stage in an industry which is of the utmost importance at the present time, and one which bids fair to increase in importance.

Products such as benzene, phenol, naphthalene, and anthracene form the starting-points in the manufacture of a host of articles in daily use, articles as widely different from each other as is the proverbial chalk from cheese. Thus we have synthetic dyestuffs, drugs, flavouring matters, scents, photographic developers, and many other substances with which we could scarcely dispense.

**DISCOVERY OF PERKIN.**—This industry may be said to owe its inception to a discovery made fifty years ago by the late Sir W. H. Perkin, then an assistant of the famous chemist Hofmann. In the course of an investigation which had for its object the artificial preparation of quinine, Perkin noticed a dark-coloured precipitate, from which he attempted to obtain colourless crystalline derivatives. Failing in this, he tried the effect of this coloured substance on silk, and found that it acted as a dye. Thus began the artificial dyestuff industry, which at the present day has grown to enormous dimensions. A vast number of investigations were at once begun, not only with the object of preparing new dyes, but also with the view of elucidating the nature of many compounds allied to benzene and its known derivatives.

**KEKULÉ'S BENZENE RING.**—A great impetus was given to these investigations by the work of Kekulé on the constitution of benzene. He suggested that this substance was best represented by assuming that the carbon atoms in the benzene molecule were united in the form of a hexagon, alternately doubly and singly linked as shown below.



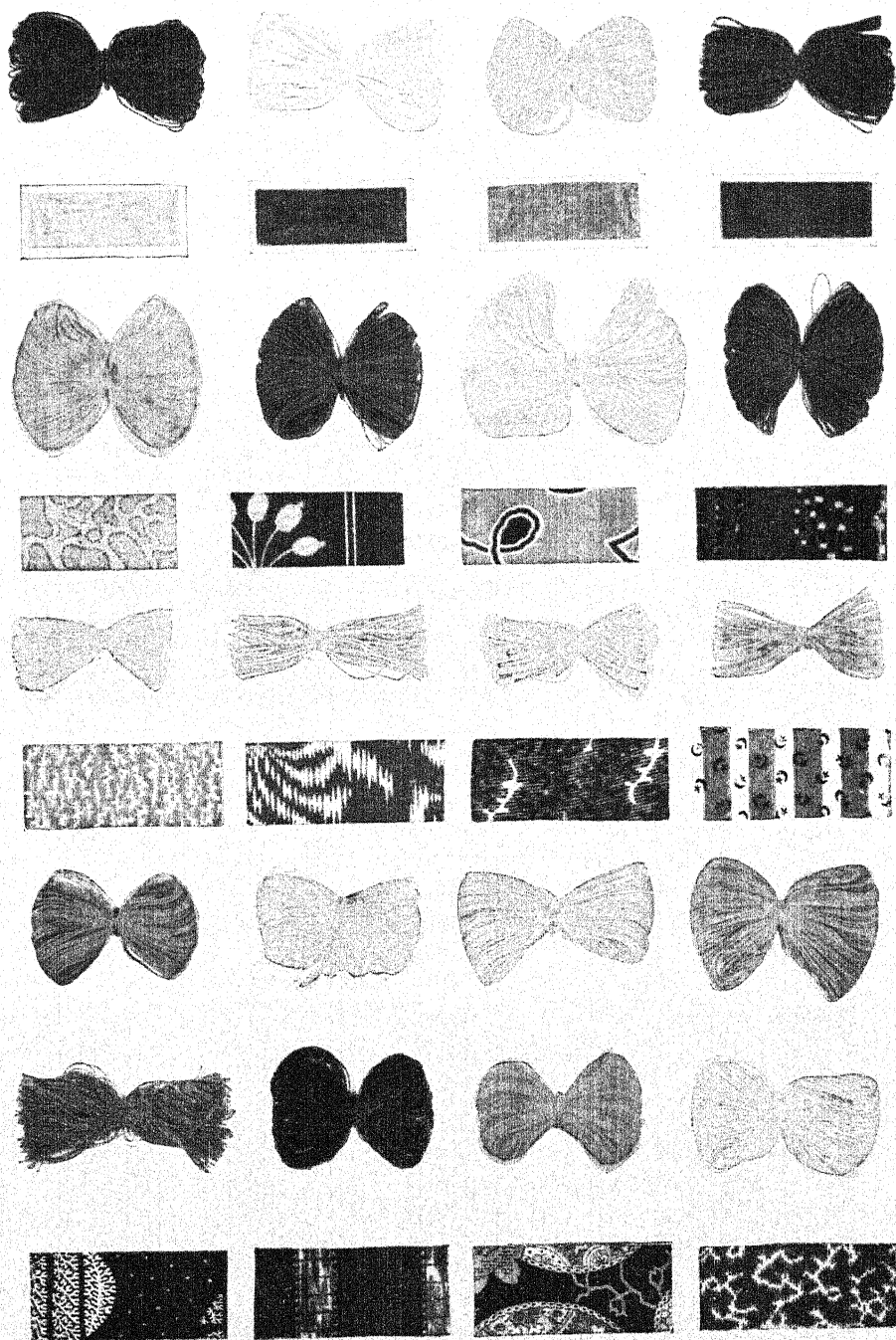
EFFECTS AND COLOURS PRODUCED ON  
DIFFERENT FABRICS BY THE USE  
OF COAL-TAR COLOURS

This plate is intended to show the extraordinary range of colours which has been rendered possible by the discovery of artificial dyestuffs. Every shade can be obtained, and patterns of every kind may be produced by the use of suitable dyestuffs.

The plate is a photographic reproduction of actual skeins of wool, silk, and cotton, and of pieces of the same materials dyed or printed with different coal-tar products.



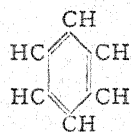




EFFECTS AND COLOURS PRODUCED ON DIFFERENT FABRICS  
BY THE USE OF COAL-TAR COLOURS





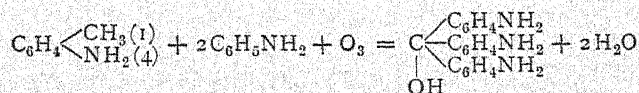


Instead of a blind search for colouring matters, research on scientific lines was now possible, and the result was that in the course of the succeeding years a vast number of new compounds became known, all belonging to the aromatic or benzene series.

It will be interesting to give here a short account of the development of the artificial dyestuff industry, though such an account must of necessity be very incomplete.

**PICRIC ACID, MUREXIDE, AND MAUVE.**—The first artificial colouring matters to be used were **PICRIC ACID** obtained from indigo, and **MUREXIDE** prepared from uric acid. On account of the costliness of the raw materials these substances could not be used to any large extent. In 1856 Perkin discovered that by the oxidation of impure aniline a violet dyestuff was obtained. Then for the first time the artificial production of a colouring matter was rendered possible, for Hofmann had discovered benzene in coal tar, his pupil Mansfield had devised a method for recovering it from this product, and it was shown later that the nitrobenzene prepared therefrom by simple nitration could readily be reduced to aniline by means of iron filings and acetic acid. Perkin used these methods for the preparation of aniline violet, or **MAUVE** as it was called.

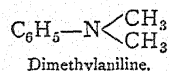
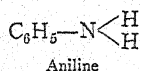
**FUCHSINE.**—Mauve or mauveine was technically so successful that other workers were incited to pursue investigations with the object of making new dyestuffs, and the first result was the discovery of fuchsine by Verguin. Hofmann showed that fuchsine was the salt of a base to which he gave the name **rosaniline**. The constitution was elucidated much later by Emil and Otto Fischer, and it was shown that Perkin owed his success to the fact that the aniline he employed was a mixture of aniline with paratoluidine. This mixture on oxidation gives **rosaniline** in accordance with the following equation:—



**ROSANILINE BLUE.**—In 1860 Girard and de Laire discovered the first artificial blue dyestuff, **ROSANILINE BLUE**, by heating aniline with **rosaniline**. This process consists in the substitution of a phenyl group for a hydrogen atom, and the importance of this was soon recognized by Hofmann, who

heated rosaniline with ethyl iodide, thereby obtaining iodine violet. By heating rosaniline with a further quantity of ethyl iodide a new dyestuff was obtained, iodine green.

The next stage in the history of these dyestuffs is marked by the employment of dimethylaniline, which, it will be seen, is aniline in which the two hydrogen atoms of the amido group have been replaced by methyl groups:



**METHYL VIOLET AND METHYL GREEN.**—The two dyestuffs thus prepared were METHYL VIOLET and METHYL GREEN, and these rapidly displaced the previously existing dyestuffs of the same colours.

**YELLOW DYESTUFFS.**—Then followed the preparation of yellow dyestuffs by the nitration of aromatic derivatives. Amongst the earliest of this class were Martius yellow and Palatine orange.

**ALIZARINE.**—Up to this time the search for new colouring matters had been an empirical one, but after the introduction of Kekulé's benzene theory investigations proceeded along rational lines. The first reward for this well-directed research went to two chemists, Graebe and Liebermann, who in 1868 succeeded in preparing ALIZARINE from anthracene. This important dyestuff is the essential constituent of the madder plant, which had previously been cultivated to a large extent for Turkey-red dyeing. These two workers, together with Caro, patented<sup>1</sup> a process for the artificial preparation of alizarine, and this process, with certain modifications, is employed to-day. It consists of the following steps.

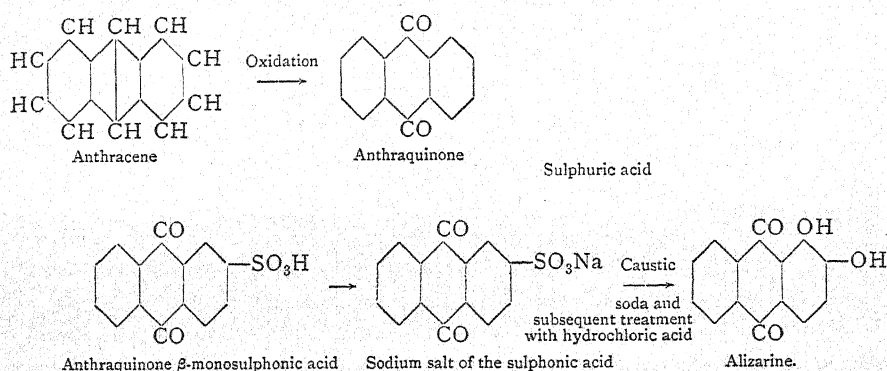
**PREPARATION OF ALIZARINE.**—Crude anthracene obtained from coal tar is first washed with solvent naphtha or pyridine to remove impurities, and then oxidized with potassium bichromate and sulphuric acid. By this means anthraquinone is formed, while the other hydrocarbons are left unchanged. The mixture is then treated with more sulphuric acid, the anthraquinone is dissolved unchanged, and the other substances are converted into sulphonic acids. On pouring the whole into water, the anthraquinone is precipitated while the acids are dissolved. The anthraquinone thus obtained is further purified by sublimation, and is then subjected to the action of fuming sulphuric acid, which transforms it into the  $\beta$ -monosulphonic acid. The acid is converted into the sodium salt, and this is fused with caustic soda for two or three days at a temperature of 200° C., a small amount of sodium chlorate being added to complete

<sup>1</sup> Perkin filed an application for a patent for the preparation of alizarine *one day after Graebe and Liebermann.*



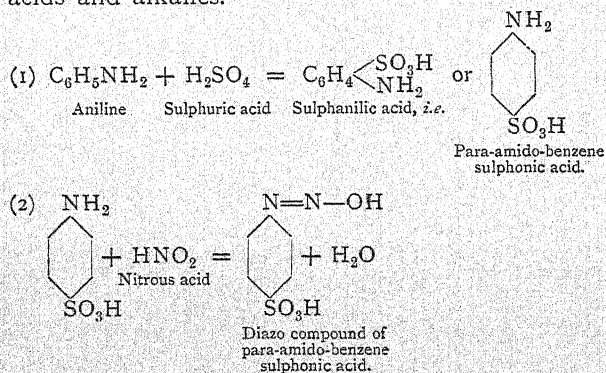
the oxidation. The fused mass is extracted with water, and the alizarine recovered by adding hydrochloric acid.

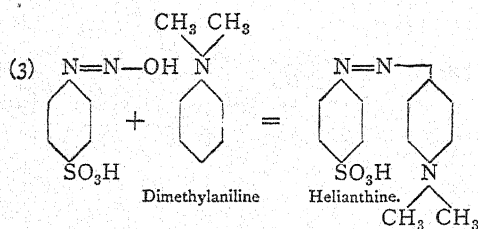
The various steps in the operation will be understood by reference to the following:—



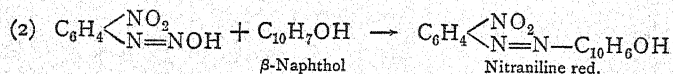
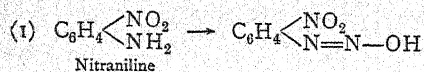
**DISCOVERY OF DIAZO COMPOUNDS BY GRIESS.**—A most important class of dyestuffs was obtained as a result of the discovery by Griess of the diazo compounds. These are made by treating an aromatic amine with nitrous acid, and then "coupling" the resulting diazo compound with either another amine or a phenol. As an example of this class of dyestuffs, the preparation of helianthine or methyl orange may be described.

**PREPARATION OF METHYL ORANGE.**—Aniline is heated for some hours with strong sulphuric acid, and the product poured into water. The sulphonic acid thus produced is then diazotized with nitrous acid, and the resulting compound "coupled" with dimethylaniline. **METHYL ORANGE** is thus obtained, and though this particular substance is not of much service to the dyer, on account of its sensitiveness, yet it is of great use to the chemist, who employs it as an indicator in the volumetric determination of acids and alkalis.



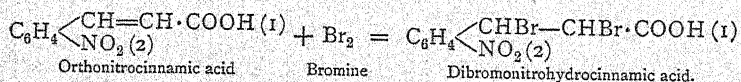


OTHER DYESTUFFS.—Next followed a series of beautiful yellow and orange dyestuffs, obtained by diazotization and “coupling” with phenols of various kinds, such as the naphthols and nitronaphthols. Later reds, and finally blacks and blue-blacks, were prepared by the use of naphthalene derivatives. An important discovery was made in connection with these diazo compounds. It was found that if the substance to be dyed were first impregnated with the amine, this diazotized on the fibre and then “coupled”, there resulted a dye of great fastness. Amongst the most valuable of these “ingrain colours” is NITRANILINE RED, produced by diazotizing nitraniline, and then combining the diazo compound with  $\beta$ -naphthol.

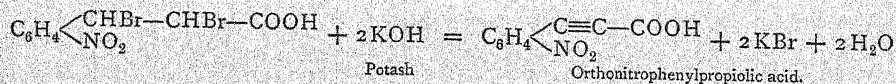


SYNTHESIS OF INDIGO BY VON BAEYER.—One of the greatest triumphs of the chemist is the synthetic preparation of INDIGO. This was first accomplished by Adolf von Baeyer in 1880. This synthesis, though not used on a commercial scale, is of the greatest interest, and is briefly as follows.

Orthonitrocinnamic acid is treated with bromine. Two atoms of bromine are added, and dibromonitrohydrocinnamic acid is formed.

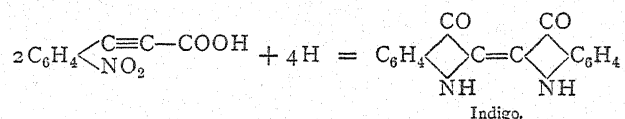


From this compound two molecules of hydrobromic acid are removed by treatment with alcoholic caustic potash, with the formation of orthonitrophenylpropionic acid.



This, on reduction with grape sugar in alkaline solution, yields indigo.





Although this process is not used for the manufacture of indigo as such, the nitrophenylpropionic acid is employed in calico printing, as the reduction to indigo can be performed on the fibre.

**SYNTHESIS OF INDIGO BY HEUMANN.**—The synthesis which has been successful on a commercial scale is the one due to Heumann. By means of it the *Badische Anilin-und Soda-fabrik* has been able to place upon the market an artificial product which can compete both in quality and price with the natural product.

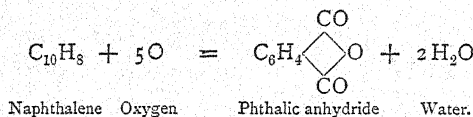
For the last twenty years the *Badische Anilin-und Soda-fabrik* has been engaged on the problem of the preparation of synthetic indigo. After an unparalleled expenditure of time and energy they have at last succeeded in their endeavours. The record of their attempts reads like a fairy tale, though each step of their process is the result of long and patient research.

**MANUFACTURE OF INDIGO.**—The raw material for this synthesis is NAPHTHALENE, a substance existing in large quantities in coal tar. At the lowest estimate 50,000 tons of naphthalene are present in the coal tar annually produced. Of this amount only 15,000 tons were formerly extracted, but so great has been the demand for this substance that the price of naphthalene has almost doubled in recent years.

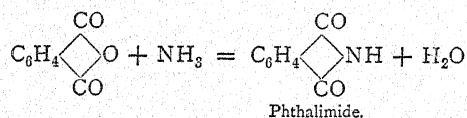
The first step is the oxidation of this naphthalene to phthalic anhydride. This can be accomplished by means of sulphuric acid and potassium bichromate, but as this method is too expensive a new process had to be devised. Such a one was found by Sapper, who discovered that if naphthalene be heated with highly concentrated sulphuric acid, in presence of a trace of mercury, there results a good yield of phthalic acid. But it was necessary to find a cheap method of preparing concentrated or fuming sulphuric acid. Had they been compelled to depend upon the old lead-chamber process, it would have been simpler to use the chromic-acid method.

Accordingly all their energies were directed towards the perfecting of a new process for the manufacture of sulphuric acid. This was found in the contact process. Sulphur dioxide and oxygen passed together over finely divided platinum, in the form of asbestos covered with a thin film of the metal, react to form sulphuric anhydride. This can be absorbed either in water or in sulphuric acid, so that an acid of any required degree of concentration can be produced. The first difficulty was therefore over-

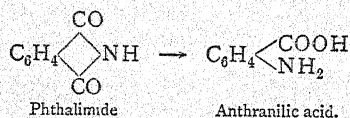
come. Phthalic anhydride could be prepared in any desired quantity at a minimum cost.



The next stage consists in the transformation of the phthalic anhydride into phthalimide. This takes place easily by treatment with ammonia.

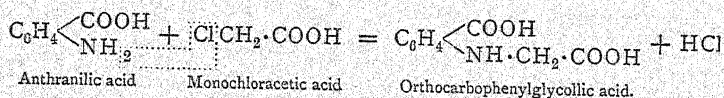


By treating phthalimide with chlorine and caustic soda it is converted into anthranilic acid.

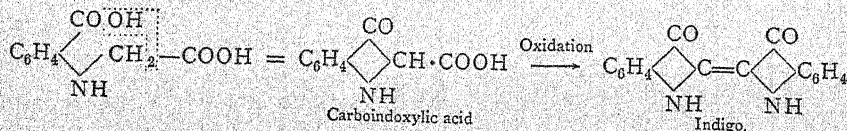


The anthranilic acid thus formed has next to be condensed with monochloroacetic acid, and the next problem to be faced was the chlorination of 2000 tons of acetic acid per annum. To effect this, another new method was necessary, since the ordinary methods for the preparation of chlorine gave a product either too expensive or too dilute for the purpose in hand. All energy was therefore devoted to the elaboration of a process which should give chlorine of suitable strength and at a reasonable cost. This was found in the electrolytic method described later. By this method chlorine was produced which met all the requirements of the case, and at the same time caustic soda was obtained as a by-product.

The anthranilic acid and the chloroacetic acid readily condense, with the formation of orthocarbophenylglycollic acid.



and this on fusion with alkali gives carboindoxyllic acid, which is changed into indigo when the alkaline solution is oxidized with a current of air.



**SULPHUR DYESTUFFS.**—An important group of dyestuffs has been



introduced comparatively recently. It includes a number of products which are known collectively as the sulphine or sulphur dyestuffs. They are mostly of unknown constitution, and owe their importance to the fact that they dye cotton directly, that is, without the assistance of a mordant.

They are usually prepared by fusing together some organic compound containing nitrogen and sulphur, with or without the addition of sodium sulphide. In this way a "melt" is obtained, from which the dyestuff is isolated. As a general rule, this is insoluble in water, but dissolves in alkalies. The dyebath is commonly prepared with sodium sulphide, the goods dyed in this, and the colour subsequently developed by oxidation.

WITT'S THEORY OF DYES.—A great deal of work has been done with the object of ascertaining to what extent the composition of a compound influences its properties as a dye. O. N. Witt has put forward a theory which has much to recommend it. According to him, there are certain groups which he calls CHROMOPHORES, which must be present in any compound that is coloured. It does not necessarily follow that a compound containing chromophores, or a CHROMOGENE as it is called, is a dye; but if in addition there is present a salt-forming group, which may be either basic (*e.g.*  $\text{NH}_2$ ) or acidic (*e.g.*  $\text{OH}$  or  $\text{SO}_2\text{OH}$ ), then the substance is a dye.

For example, nitrobenzene is a chromogene, since it contains the chromophore grouping  $\text{NO}_2$ . It is, however, not a dye. If we introduce into the molecule an oxy group, the resulting nitrophenol can give salts, *e.g.* the sodium salt, which can act as dyestuffs.

The presence of certain groups has a marked influence upon the colour of the dye. For example, the introduction of the sulphonic group has usually the effect of weakening the dye; but, on the other hand, it confers upon the substance the valuable property of being soluble in water. When chlorine is substituted in the molecule it is found that the dyeings have a bluer tinge than the original dye.

The carboxyl group has little effect on the shade of the dyestuffs, but it increases the fastness of the dyeings.

THEORIES OF DYEING.—There are two main theories as regards the nature of the process of dyeing. The first is a chemical one, and teaches that the process must be regarded as one of combination between the basic or acidic constituents of the fibre with the acidic or basic dyestuffs. The second maintains the view that it is essentially a mechanical process depending upon osmosis, so that the dyed fabric may be looked upon as a solid solution.

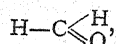
In addition to dyestuffs, a great variety of other products is obtained

from the substances isolated from coal tar, which will be mentioned in their proper connection.

With the great development of chemistry a vast number of new substances have been discovered which are of the greatest use in medical and surgical practice as antiseptics or drugs, and of these the most important will be mentioned below.

### ANTISEPTICS

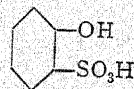
FORMALDEHYDE.—This substance, which has the constitution



is prepared by the oxidation of methyl alcohol or wood spirit. It is generally sold in the form of a 40-per-cent solution under the name of **FORMALIN**, and is used as a disinfectant, and to some extent as an antiseptic. It is also of great value in preserving certain animals and animal tissues for scientific purposes.

**ODOFORM**.—This compound is tri-iodo methane, and is theoretically derived from the hydrocarbon methane by the substitution of three atoms of hydrogen by three atoms of iodine. It was formerly prepared by heating a solution of iodine in alcohol with sodium carbonate. It crystallizes in yellow hexagonal plates, and has a peculiar and characteristic odour. Recently an electrolytic method for its preparation has been introduced. A current is passed through a solution containing potassium iodide, alcohol, and sodium carbonate at a temperature of 65° C. In this way about 80 per cent of the iodide is converted into iodoform.

**ASEPTOL**.—This is orthophenolsulphonic acid, obtained by treatment of phenol with concentrated sulphuric acid. It is sometimes sold under the name **sozolic acid**. A di-iodo derivative of the para sulphonic acid of phenol is also used as an antiseptic, its trade name being **SOZOIODOL**.

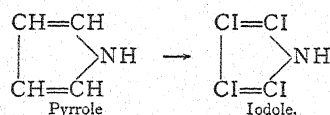


Orthophenolsulphonic acid or aseptol.

**SALOL**.—This is phenyl salicylate, prepared by the action of an acid chloride, such as phosgene ( $\text{COCl}_2$ ), upon a mixture of phenol and salicylic acid. By the use of other phenols similar compounds are obtained, all of which are good antiseptics.

**IODOLE**.—By the action of iodine and an alkali on pyrrole, a constituent of coal tar, tetraiodopyrrole is formed, and this, under the name of iodo-**le**, is largely used as a substitute for iodoform.





In addition to the above-mentioned compounds there is a considerable number of other substances which have antiseptic properties. Thymol, a constituent of oil of thyme,  $\beta$ -naphthol, naphthalene, resorcline, and many other substances, are applied either as general disinfectants or for some particular purpose.

### DRUGS

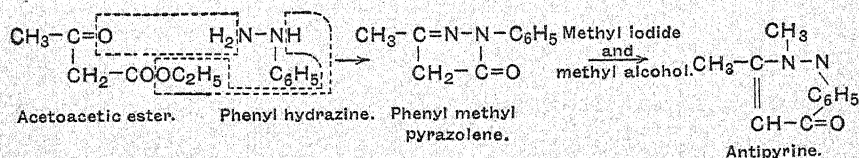
The name of the synthetic drugs is legion. Space does not permit of the mention of more than a few of the more important ones.

ETHYL NITRITE ( $\text{C}_2\text{H}_5\text{—ON=O}$ ) is used in medicine as a remedy for colds. It is generally known as "sweet spirits of nitre".

AMYL NITRITE ( $\text{C}_5\text{H}_{11}\text{—O—N=O}$ ), a pale-yellow liquid with a peculiar smell, is employed in cases of *angina pectoris*, since it produces dilatation of the blood-vessels. It is prepared from nitrous acid and amyl alcohol, obtained from the fusel oil formed when alcoholic fermentation is the result of the action of a certain species of yeast (*Saccharomyces ellipsoideus*).

CAFFEINE.—This constituent of the coffee and tea plants has already been mentioned in connection with the products synthesized by living matter. It is prepared artificially from uric acid derivatives according to the method of Fischer.

ANTIPYRINE (OR PHENAZONE).—This is a substance which has taken a prominent place in medicine. It was discovered by Knorr in 1883 in the course of an investigation, the object of which was the synthetical preparation of quinine. It is obtained by the action of phenyl hydrazine on acetoacetic ester (and subsequent treatment). The latter substance is prepared from ethyl acetate by treatment with metallic sodium, and the former from aniline by reduction. The following scheme shows how the compound is formed, and also its structural formula:—

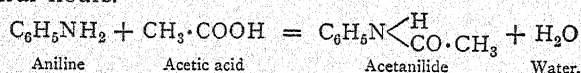


Its action is that of a febrifuge, and as such it is largely used.

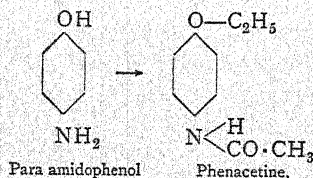
ANTIFEBRINE.—The discovery of this drug was the result of an accident. It occurred in the following manner: "Kahn and Hepp, two physicians connected with the University of Strasburg, were on intimate

terms of friendship with a chemist of the Hoechst Works, where Knorr's antipyrine was being manufactured, and requested him to send them some chemically pure naphthalene, which they desired to use internally in the case of a patient suffering with some skin disease. They received the substance, and on administering it found that while it failed to exhibit the expected effect, it promptly reduced the existing fever. When the supply of naphthalene was almost exhausted they wrote for a further quantity. To their great astonishment the second supply, unlike the first, did not manifest any antipyretic action, and on comparing the two they soon discovered that a mistake had occurred somewhere. An investigation showed that when the first request was received the laboratory boy was directed by the chemist to fill a bottle with naphthalene, but through an error some acetanilide was sent instead. The second time the chemist himself filled the bottle correctly. Thus, through an accident, acetanilide was introduced to medicine, a remedy which to-day is used by the ton as an antipyretic and antineuralgic; and through the irony of fate the most powerful competitor of antipyrine was discovered as the result of a mistake made in the very factory which was realizing enormous profits from the production of antipyrine."<sup>1</sup>

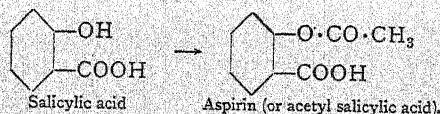
Acetanilide is prepared by heating together aniline and glacial acetic acid for several hours.



PHENACETINE.—This is also used as a remedy in neuralgia. It is derived from para amidophenol by substitution of the hydrogen of the oxy-group by the ethyl radical, and of one hydrogen atom of the amido group by the acetyl group.



ASPIRIN.—When salicylic acid is treated with acetic anhydride the hydrogen of the oxy group is replaced by the acetyl radical, and the resulting product is known by the name of aspirin. It is used as a febrifuge.



<sup>1</sup> *Schweitzer*. Lecture given in commemoration of Sir W. H. Perkin's jubilee.



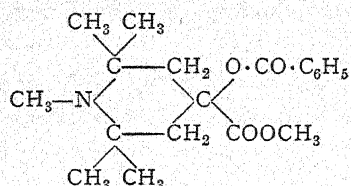
## ANÆSTHETICS, SOPORIFICS, ETC.

Various halogen derivatives of the paraffins are used as anæsthetics. Some, for example METHYL CHLORIDE ( $\text{CH}_3\text{Cl}$ ), are used as local anæsthetics; others, such as CHLOROFORM ( $\text{CHCl}_3$ ) and METHYL CHLOROFORM ( $\text{CH}_3 \cdot \text{C} \cdot \text{Cl}_3$ ), are of general service. Amongst the class of anæsthetics ETHER must be mentioned. This is frequently given with alcohol and chloroform, or with nitrous oxide (laughing gas).

COCAINE.—Is largely used as a local anæsthetic. It is a naturally occurring alkaloid, and was isolated by Gädeke in 1855 from the leaves of the coca plant (*Erythroxylon Coca*).

EUCAINE.—This is a synthetic product discovered by Merling. For most purposes it can be substituted for cocaine, and it is claimed that while it is equally powerful as an anæsthetic, it is much less toxic.

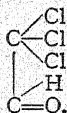
The constitution is shown by the following formula:—



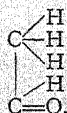
Tetramethyl-*n*-methyl- $\gamma$ -benzoxypiperidin- $\gamma$ -carbonic acid ester or eucaine.

Still more recently various anæsthetics have been suggested for use in place of cocaine. Amongst them may be mentioned MYDRIATICUM or EUPHTHALMIN, STOVAINE, and NOVOCAINE, though whether these have any great advantage over the natural product remains yet to be proved.

Of the soporifics used, CHLORAL HYDRATE is one of the most common. It is prepared by the action of chlorine upon ethyl alcohol, and has the composition

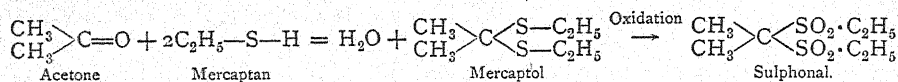


It will be seen that it is a trichlor derivative of acetaldehyde,

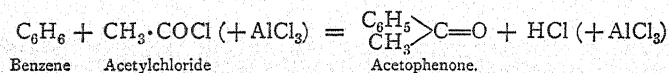


SULPHONAL.—This is a compound formed from acetone and mercaptan

by treatment with hydrochloric acid and oxidation of the product. Its constitution will be seen from consideration of the following formulæ:—

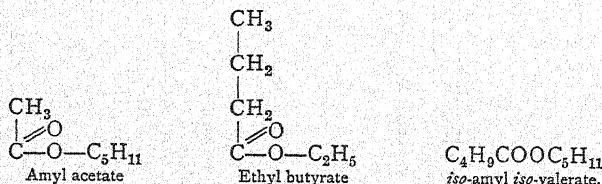


**HYPNONE.**—This is acetophenone, a ketone containing both an aromatic and a fatty radical. It is obtained by the action of aluminium chloride upon a mixture of benzene and acetyl chloride, according to the following equation:—

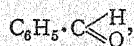


### FLAVOURING MATTERS, ETC.

Many compounds of the fatty acids with the alcohols of the same series are characterized by possessing pleasant flavours, and these substances are used to a considerable extent in cookery and confectionery at the present day. For example, the amyl ester of acetic acid, or **AMYL ACETATE**, is largely employed as essence of jargonelle pears. The ethyl ester of butyric acid has a flavour closely resembling that of pineapples, and *iso*-amyl *iso*-valerate is known commercially as **APPLE-OIL**.

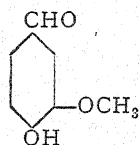


In the aromatic series **VANILLIN**, the essential constituent of vanilla, has been synthetically prepared; **BENZALDEHYDE**,

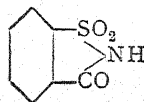


has to a great extent replaced the oil of bitter almonds formerly obtained from the plant product; for certain purposes **SACCHARINE** forms an excellent substitute for sugar, particularly in cases of *diabetes mellitus*, where the taking of cane sugar or of starchy foods is prejudicial to the health of the patient. These and many other substances are now obtainable in the laboratory, and in many cases the starting-point in their manufacture is the complex mixture coal tar, formerly a nuisance, now a most valuable asset.





Methoxyhydroxybenzaldehyde or vanillin

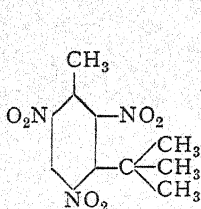


Orthosulphobenzimide or saccharine.

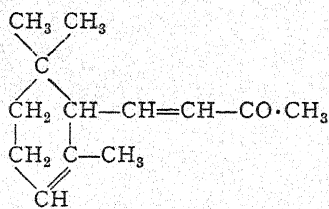
## PERFUMES

The manufacture of artificial perfumes has undergone a vast change with the development of synthetic chemistry. Long before the introduction of Perkin's mauve, nitrobenzene had been used to some extent for the scenting of soaps under the name of OIL OF MIRBANE. The odour recalls that of oil of bitter almonds, though it is not so delicate.

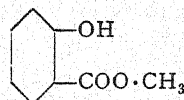
To-day almost every fragrant odour can be imitated successfully, and we have artificially prepared musk, violets, roses, heliotrope, jasmine, wintergreen, new-mown hay, and many other delicious perfumes.



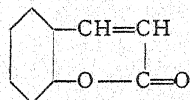
Trinitrobutyltoluene or artificial musk



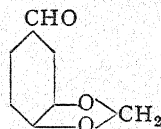
Ionone (essence of violets)



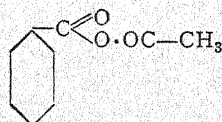
Methylsalicylate or oil of wintergreen



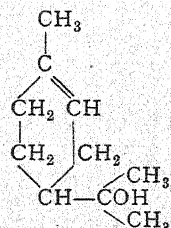
Coumarin (new-mown hay)



Piperonal (heliotrope)



Benzyl acetate (jasmine)



Terpineol (white lilac).

## EXPLOSIVES

In addition to the ordinary gunpowder known for so many centuries, modern chemistry has given us a wide range of explosives. By treating a mixture of alcohol and nitric acid with metallic mercury, a compound known as FULMINATE OF MERCURY is formed. This, by reason of its property of exploding when struck, is used in the manufacture of percussion caps.

NITROGLYCERINE, one of the most powerful of explosives, is obtained by acting upon glycerine with a mixture of nitric and sulphuric acids. The name is a misnomer, as it is really not a nitro-derivative but a nitrate. For convenience of handling it is generally mixed with a siliceous earth called *kieselguhr*, and in this form it is known as DYNAMITE. Dynamite is always caused to explode by means of fulminate of mercury, and it is supposed that the explosion takes place as the result of what is known as "mechanical shock". The molecule of the fulminate is regarded as being in a very unstable state, and when the equilibrium is disturbed, as by a blow, there is set up in the molecule of the nitroglycerine a similar state of unrest, with the result that a sudden decomposition occurs.

GUN-COTTON.—When cotton wool or cellulose is treated with a mixture of nitric and sulphuric acids, a substance known as GUN-COTTON is produced. This when dissolved in acetone and mixed with various other substances, such as camphor, and then allowed to partially dry, forms a valued explosive known to the world as CORDITE.

LYDDITE, another well-known substance, is a derivative of phenol. It is closely allied to picric acid (trinitrophenol), a substance prepared from carbolic acid and nitric acid.

Enough has been said to show that chemical science has indeed proved herself to be the handmaid of the various arts. Without her aid many things which are to-day possible would have been unattainable. The knowledge of the behaviour of chemical compounds has rendered practicable far more than was dreamt of in the philosophy of fifty years ago. Without chemistry we should be wanting in all the refinements of modern photography; we should lack the thousand-and-one tints that meet the eye on all sides; and surgery and medicine would be the poorer by many valuable means for the alleviation of human suffering.



## CHAPTER VII

## THE CHEMISTRY OF DAILY LIFE

## GLASS

GLASS is a complex mixture of silicates of the alkalies and alkaline earths, though in special cases borates and phosphates may take the place of the silicates.

In the form of window glass it was first made in England in the year 1557 at Crutched Friars, London, though later fine work like the Venetian glass was manufactured at Savoy House.

MANUFACTURE OF GLASS.—The materials of which the glass is made are melted in crucibles of fireclay which are placed in reverberatory furnaces. Formerly the furnace was heated by either solid or gaseous fuel, but of recent years electric furnaces have been introduced. Two of the most successful of these are the Voelker and the Becker types, in which the materials are made to fuse by means of a current passed between carbon anodes.

KINDS OF GLASS.—There are many different kinds of glass, such as crown, sheet, window, plate, bottle, and lead glass, in addition to the numberless varieties of glass used for optical purposes. These different kinds owe their peculiar properties to the variation in the proportions of the constituents. A few examples may be given of the formulæ of the chief kinds.

CROWN GLASS.—Silica (sand), 400 parts; quicklime, 64 parts; sodium sulphate, 200 parts; charcoal, 16 parts.

PLATE GLASS.—Silica, 400 parts; sodium carbonate, 250 parts; chalk, 30 parts.

WINDOW GLASS.—Silica, 120 parts; potassium carbonate, 60 parts; arsenic, 1 part; borax, 2 parts.

LEAD (CRYSTAL) GLASS.—Silica, 340 parts; potassium carbonate, 110 parts; red lead, 220 parts; manganese oxide,  $\frac{1}{2}$  part; nitre, 20 parts.

BOTTLE GLASS.—Silica, 100 parts; potassium carbonate, 20 parts; sodium sulphate, 15 parts; chalk, 5 parts.

OPAL GLASS.—Silica, 100 parts; red lead, 120 parts; arsenic, 4 parts; potassium carbonate, 30 parts; borax, 4 parts; calcium phosphate, 14 parts.

CROWN GLASS.—In the manufacture of crown glass a globular mass of the molten material is attached to the end of a metal pipe. By alternate rotation and holding in a vertical position, the glass is made to assume the form of a sphere. It is then placed upon a flat iron table, and by blowing

through the pipe it is gradually flattened until a sheet is obtained. This method has been largely replaced by one which produces what is known as sheet glass. In this process the glass is made to assume the form of a cylinder, which is cut open and then rolled out flat.

PLATE GLASS is made by pouring out the molten glass on to a flat metal plate, and rolling out the mass to an even thickness. The plate thus obtained is ground down to the desired thickness, and is then polished between rollers, rouge—that is, oxide of iron—being added.

In all cases the glass, after slight cooling, requires to be well annealed; that is to say, the temperature must be allowed to fall to that of the atmosphere by very slow degrees.

OPAL GLASS is made by adding to the ordinary melt calcium phosphate, fluor-spar, cryolite, or various other substances. Coloured glasses are made by the addition to the melt of various substances. For example, rose-coloured glass owes its colour to the presence of minute quantities of gold salts. Red or ruby glass is made by adding either copper or antimony compounds; blue glass, by adding cobalt salts; violet, by adding manganese oxide; green glass, by adding chromium oxide or bichromate of potash; yellow, by adding uranium salts; &c.

As may be gathered from the foregoing recipes, it is impossible to assign any definite formula to glass, although Dumas thought that



represented the composition of most of the specimens he examined.

In certain glasses potassium replaces sodium to a greater or less degree, and these are generally much harder and more infusible than the soda glasses. An increase in the percentage of silica has the same effect, and a greater proportion of lime renders the glass more resistant to chemical action.

Comparatively recently vessels for chemical operations have been made of fused quartz. For many purposes these are likely to be exceedingly useful, as they are less liable to crack by heat, and are far more resistant to the action of acids, alkalies, and other chemicals, than are vessels made of even the best glass.

#### PORCELAIN AND EARTHENWARE

CLAY.—All earthenware and porcelain goods are made from CLAY. This is a product of the weathering of rocks, and consists mainly of a mixture of silicates. The silicates are produced by the weathering of the



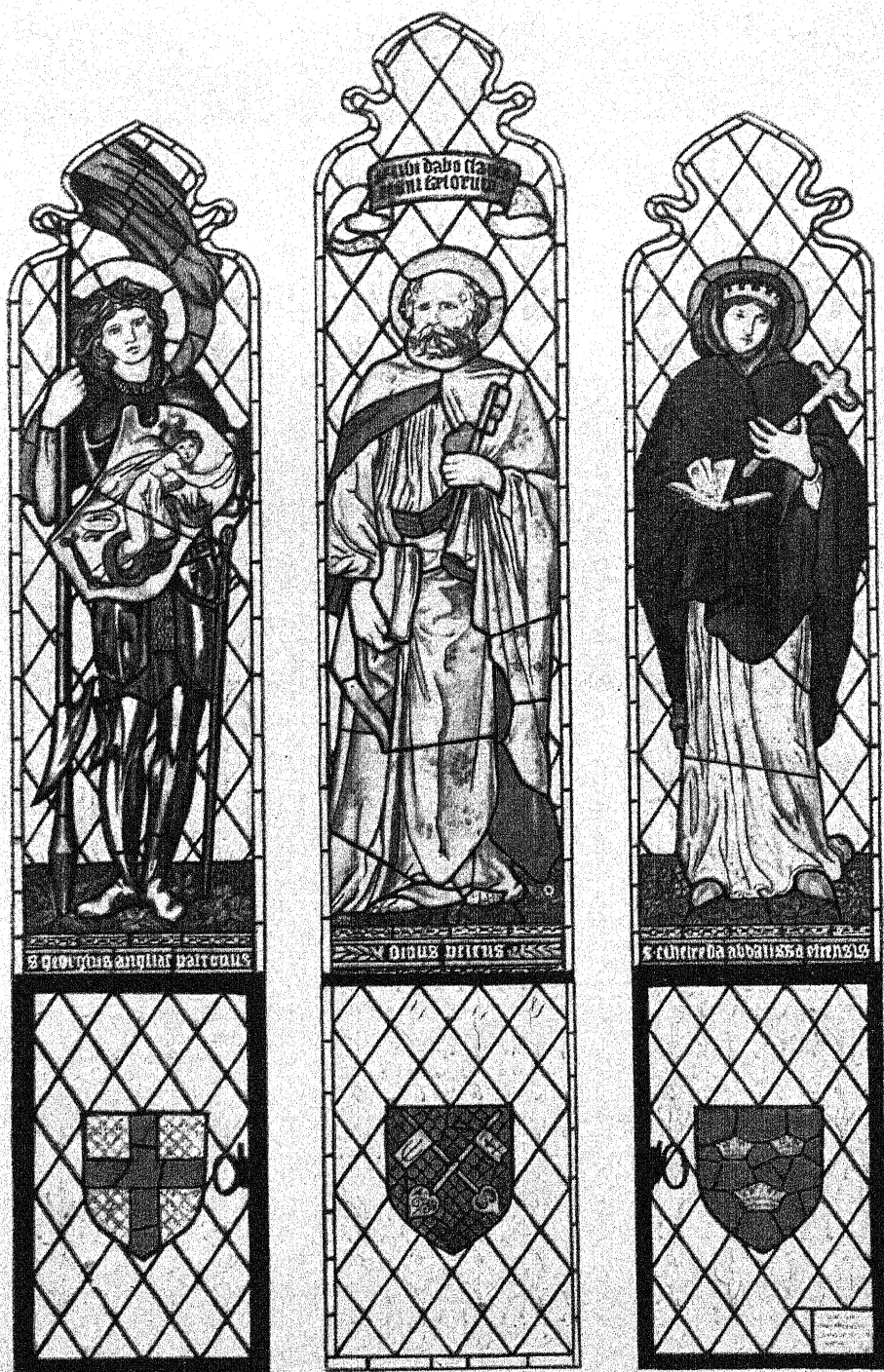
A WINDOW IN THE COMBINATION ROOM OF  
PETERHOUSE, CAMBRIDGE

(By the kind permission of the Master and Fellows)

This is an excellent example of the results obtained by the use of transparent pigments in modern glass. In this case Morris glass has been used, and the design is in part due to Burne-Jones.







A WINDOW IN THE COMBINATION ROOM OF PETERHOUSE, CAMBRIDGE





felspars, and the finest kinds are those in which the quartz is absent, so that the resulting mass consists principally of aluminium silicate.

KAOLIN.—For the finest kinds of china a pure white clay known as kaolin is used. This is found in granite districts where the felspathic constituents have been so altered by atmospheric agency that the result is a fine, white, smooth powder.

MANUFACTURE.—In all earthenware manufacture the clay is made into a paste with water, moulded to the required shape, and then heated or burned until the mass sets hard. By the introduction of iron and other constituents the baked ware can be made to assume various colours.

GLAZING.—The ware so made is porous, and for ordinary purposes it is necessary to render this impervious to water. The porous matter, or *biscuitware* as it is called, is *glazed*. This is accomplished in various ways, the four principal ones being the following.

1. EARTH GLAZINGS.—These are transparent, and are formed by the fusion of silica and the alkalis, together with a certain amount of alumina.

2. LEAD GLAZES.—The articles to be glazed are dusted with a powder containing oxide of lead, and then baked. A transparent coating is the result.

3. ENAMEL GLAZES.—These are semi-opaque, and are made by mixing with lead oxide a certain proportion of tin oxide.

4. LUSTRES.—These are formed by the volatilization of a substance such as common salt. In the kiln in which the goods are burned salt is placed, and this on strongly heating is converted into a state of vapour, so that the biscuitware is glazed both inside and out.

The COLOURING OF PORCELAIN is similar to the colouring or staining of glass. The design is painted upon the biscuit, which is then burned, so that the colours become fast and bright.

The pigments are all mineral substances, and include cobalt oxide for blue, gold salts for purple and rose, iron compounds for reds, chromium oxide for green, lead and barium chromates for yellow, &c.

BRICKS AND TILES.—Another branch of the earthenware industry is the manufacture of bricks, tiles, &c. The principles of the process are the same as in the making of porcelain and pottery generally. The clay is kneaded with water, moulded into the required shape, and then burned in kilns.

## PAPER

Formerly all paper was made from rags—the best from linen, the inferior qualities from cotton. To-day the finest kinds of paper are still made from linen rags, but it is usual to add also other materials.

MANUFACTURE.—The first process in the manufacture of linen paper is the sorting of the rags. Five main classes are recognized, viz. *superfines*, which are clean and white; *outshots*, which are less clean; *seconds* and *thirds*, still less clean; and, finally, *prints*, which are coloured.

After this sorting they are well beaten to remove all dust, cut into pieces about 4 in. square, and then placed in boilers with a solution of caustic soda, the amount of the latter added being about 1 to 6 per cent of the weight of the rags. With this solution they are boiled for a time varying from two to twelve hours under a pressure of 15 to 20 lb. per square inch. They are then washed thoroughly to remove all traces of alkali, and in this state are known as *half-stuff*. The subsequent treatment is the same as is described below.

For cheaper kinds of paper, materials other than rags are used. One of the most common of these is ESPARTO, a grass obtained from certain parts of Spain and North Africa. This, too, is converted into *half-stuff* by boiling with caustic soda.

Much of the inferior paper is now made from WOOD PULP. Two methods of treating the wood are in use, the mechanical and the chemical.

1. MECHANICAL WOOD PULP.—This is made by forcing the wood against rapidly revolving sandstones. For this purpose poplar, aspen, spruce, and fir are best adapted.

2. CHEMICAL WOOD PULP.—For this kind of pulp coniferous woods are generally employed. There are two principal methods of dealing with the wood.

(a) THE BISULPHITE METHOD.—In this process the wood is first cut into chips, and these are boiled with a solution of bisulphite of lime or magnesia for a period varying from eight to seventy-two hours under a pressure of seven atmospheres.

(b) THE SODIUM SULPHATE METHOD.—The wood chips are boiled under pressure with a strong solution of sodium sulphate. This is the most economical of all the processes of obtaining paper from wood, inasmuch as the sodium sulphate is comparatively inexpensive, and can further be, to a large extent, recovered after use.

The *half-stuff*, however obtained, is first bleached, generally with chlorine, and then put into a *beater*. This consists of an iron trough



which is made in the form of a dish. Running in this trough is a heavy roller, to which are attached knives which cut the fibres, and at the same time help to beat the pulp into a felted mass. When this is accomplished, resin is added and, finally, alum, these materials serving to size the paper and so to render it non-absorbent.

**DYEING.**—Paper is dyed either with mineral colours, such as lead chromate, Prussian blue, &c., or with artificial dyestuffs. Paperhangings are dyed in the same way as is done in the case of calico printing.

**PARCHMENT PAPER** is made by passing unsized paper through a solution of zinc chloride or through sulphuric acid, followed by a bath of ammonium chloride. The paper is then washed, dried, and polished by being passed over smooth rollers.

### ARTIFICIAL SILK

**AUDEMARS' PROCESS.**—More than 150 years ago Réaumur suggested the possibility of preparing fibres which should resemble those produced by the silkworm. In 1855 a patent was taken out by Audemars for the preparation of a substance resembling silk. The process patented was briefly as follows. The bast cellulose of mulberry twigs was bleached, treated with nitric acid, and the resulting nitrocellulose dissolved in a mixture of alcohol and ether. To the solution of collodion thus made was added one of indiarubber in ether. By dipping into this solution a steel point, and then raising it, a thread was formed which hardened in the air, and could then be wound upon a winch.

**PROCESSES OF SWAN AND CHARDONNET.**—After the preparation of fibres by the Swan method of squirting a solution through small apertures, a large number of processes were devised for the production of artificial silk. In some cases cellulose was nitrated, squirted through apertures, and then treated with ammonium sulphide in order to render it non-explosive; in others the cellulose was dissolved in a solution of zinc chloride. In 1855 Chardonnet introduced the first product which may be said to have been successful. According to his method, nitrocellulose is dissolved with some organic base such as aniline in alcohol and ether. Stannous chloride is added to reduce the nitrocompound and render it non-explosive.

**DU VIVIER'S PROCESS.**—Later were introduced numerous methods similar to the preceding, but differing from it in the nature of the solvent employed for the nitrocellulose and in the accessory substances added for the purpose of strengthening the fibre. For example, Du Vivier (1889) made silk from a mixture of the three following solutions: Nitrocellulose

in glacial acetic acid, gutta percha in carbon bisulphide, and fish glue in acetic acid. These are mixed, and the solution squirted in the usual manner.

**TURGARD'S PROCESS.**—Turgard, in 1904, patented a process in which nitrocellulose, albumen, and castor oil are dissolved in a mixture of alcohol and glacial acetic acid. The solution thus formed is squirted into a 1-per-cent solution of alum, which coagulates it.

**OTHER METHODS.**—An interesting method differs entirely from the foregoing. It consists in dissolving celluloid scraps and naphthalene in acetone. The solution so obtained is mixed with precipitated sulphate of barium, and then forced into sulphuric acid.

Another and important method for preparing artificial silk depends upon the fact that cellulose is soluble in a solution of copper sulphate containing an excess of ammonia. When such a solution is forced through fine openings into dilute sulphuric acid, the ammonia is neutralized and the cellulose is coagulated. This method was first introduced by Despaissis in 1890, but since that time it has undergone many modifications. One of the most important of these is that discovered by Linkmeyer in 1905. He found that if the threads prepared, as described above, were treated with caustic soda, and then dried under tension, the resulting fibre possessed a much greater lustre.

Many other substances have been proposed for the manufacture of artificial silk, such as egg albumen, casein, gelatine, which are dissolved and then treated with such compounds as formaldehyde and potassium bichromate.

## LIGHTING

**CANDLES.**—The most simple source of light is the candle. About the beginning of the fourth century wax candles were first made. In the twelfth century tallow was used for their preparation, spermaceti was introduced early in the eighteenth century, and then at a later date stearine and paraffin came into use. The principle of this kind of illuminating material is quite simple. The wick serves as a means of leading the combustible material, whether it be wax, stearine, or paraffin, to the point where it is burned.

**LAMPS** differ from candles, inasmuch as the fuel is already in the liquid form, and merely has to be conducted to the place where it is oxidized by the oxygen of the air.

In the earliest forms of lamps, such as those used by the Romans, fatty oils like colza, rape, olive, and poppy oils were used. These burn with a



smokeless flame, and it was not until the introduction by Quinquet of the lamp glass or chimney that the burning of any other oils but these was rendered really practicable. By using a chimney a draught is created and more complete combustion is obtained, so that the flame is not a smoky one. The fatty oils contain a smaller proportion of carbon, so that they may be used without a chimney, as the flame is not smoky from the presence of small particles of unoxidized carbon.

With the development of the paraffin industry the importance of the fatty oils greatly diminished, and at the present time practically all lamps are constructed to burn mineral oils.

COAL GAS.—With the introduction of coal gas the lighting industry entered upon a new phase. Great improvements were made in the quality of the gas, impurities such as sulphuretted hydrogen were removed, and for a time lighting by gas had complete sway. When, however, electricity came to be applied to the same purpose, it seemed as though gas as a lighting medium had had its day. When Auer von Welsbach discovered the fact that the oxides of certain of the rare earths possessed the property of becoming incandescent when heated, the gas-lighting industry took a fresh lease of life.

MANTLES.—The process of making the "mantles" of these earths is exceedingly simple. "Stockings" are woven of cotton, silk, and other materials. These are impregnated in a solution of salts of the rare earths, and allowed to dry on glass moulds. An asbestos cord is then threaded through one end and drawn over so as to form a loop by which the mantle can be suspended in the flame. When dry, the "stocking" is held in the flame of a pressure burner, the cotton or other fabric is burned away, leaving a skeleton of oxide. For convenience of packing and transit this fragile skeleton is dipped into a solution of collodion in ether and alcohol, to which a small amount of castor oil has been added. On removing the mantle from the solution, and allowing to dry, a thin film of collodion is left, and this serves to protect the otherwise delicate structure from breaking.

At first the substances used for this purpose were the nitrates of lanthanum, zirconium, and yttrium; but later it was found that better results were obtained with thorium nitrate containing 1 per cent of cerium nitrate. If too much cerium is present, then the light has too red a cast. The presence of the proper amount of cerium gives a whiter light, and also serves to strengthen the mantle.

The most fragile part of the mantle is the top, where the asbestos thread is inserted. There are various devices for overcoming this weak-

ness, one of the most successful being the painting of this particular part with a solution of salts of aluminium, calcium, &c.

**ELECTRIC LAMPS.**—The two chief kinds of electric lamps are the ARC LAMP and the GLOW or INCANDESCENT LAMP. In the former two carbon poles are brought into fairly close proximity and a current passed. An arc is formed, and the carbons are raised to incandescence.

In the incandescent lamp a filament of high resistance is heated by the passage of the current, and so becomes incandescent.

**LAMPS OF EDISON AND SWAN.**—The pioneers of this form of lamp were Edison and Swan, the former working with platinum, and the latter with carbon. Although Edison achieved wonderful results with platinum, this metal had eventually to be abandoned on account of its expensiveness, and also because it would not stand the temperature required for any great length of time. The carbon filament reigned supreme for some time. Methods of manufacture were improved; instead of carbon filaments obtained by charring splinters of bamboo, &c., chemically pure carbon was obtained by the carbonization of fine threads of a concentrated solution of cane sugar, &c. These filaments are sealed in a vacuum glass globe of the familiar shape, connection with the wires being made by means of small pieces of platinum.

**"CRUTO" LAMP.**—Attempts were made to find some substitute for carbon. Silicon and boron were tried without any great success, and then came the "Cruto" lamp. This is supposed to have been made by heating a platinum wire electrically in the vapour of some hydrocarbon, so that a deposit of carbon was formed on the wire. Some of the platinum was then volatilized, leaving a filament with a rather low specific resistance.

**NERNST LAMP.**—Quite a new departure was taken by Nernst in the introduction of metallic filaments. In the Nernst lamp thin rods of yttria and zirconia were heated to incandescence, but as oxygen is given off at the anode a vacuum globe cannot be used.

The first difficulty to be overcome was that of making the rods conductors. By dipping the rod in a solution of chloride of platinum, and then heating, a film of platinum was formed on the surface, which was sufficient to make the rod act as a conductor. In this way the lamp could be made to light up once; but during the process the platinum melted and ran into globules, so that on the second occasion the lamp refused to light. Eventually the problem was solved by winding a very fine platinum wire round a thin kaolin thread.

**VON WELSBACH LAMP.**—Next came the osmium lamp of Von Welsbach. In this case, too, an open globe is required; and as the vapour



of osmium which is given off is poisonous, and very hurtful to the eyes, the lamp has had no great success for indoor lighting.

**TANTALUM LAMP.**—The most remarkable of all the metallic-filament lamps was the tantalum lamp. Until there was a demand created for this metal it was only known in the form of a powder, but now it is possible to prepare it in a homogeneous state.

**KUZEL'S PROCESS.**—It will be remembered that Bredig was successful in making colloidal solutions of metals by forming an electric arc under water. Kuzel has applied this method to the manufacture of metallic filaments. The colloidal solution is made, mixed with gum tragacanth, and then squirted through fine nozzles. The filaments so formed are then heated electrically until they fuse and form a continuous wire.

Other refractory metals, such as tungsten, have been suggested for use in incandescent lamps, and it is extremely probable that in the future these metallic filaments will play an important part in electric lighting.

Mention must be made of the **MERCURY LAMP**. In this an arc is formed between two anodes in an atmosphere of mercury vapour. The resulting light is extremely rich in the violet and ultra-violet rays—the so-called *actinic rays*—and consequently the lamp is found useful in scientific research where light of this kind is frequently necessary.

## PETROLEUM

**NATURE AND ORIGIN.**—Petroleum is the name given to a variety of oils obtained from different sources, such as crude petroleum, peat, schists, shales, coals, &c.

Petroleum as it is found naturally is a mixture of hydrocarbons, and to account for its origin many theories have been propounded. These may be divided into two classes, those which assign an inorganic origin and those which regard it as the product of the decomposition of animal and vegetable remains.

**MENDELÉEFF'S VIEW.**—Mendeléeff ascribed the origin of petroleum to the action of water upon the carbides of iron present in the interior of the earth. Berthelot, on the other hand, regarded the formation of petroleum as being due to the action of water containing carbon dioxide on the alkali metals, which latter he supposed were present in the molten mass.

**VIEW OF HOEFER AND ENGLER.**—As opposed to these views are those maintained by Hofer and Engler, who look upon petroleum as being mainly derived from organic remains. Engler has obtained, by

the distillation of fish oil under great pressure, a product resembling in a very marked manner the ordinary petroleum of natural origin.

ARTIFICIAL PETROLEUM OF SABATIER AND SENDERENS.—Two French chemists, Sabatier and Senderens, have succeeded in preparing a mixture of hydrocarbons very similar in character to the natural petroleum, by passing acetylene over finely divided nickel. By regulation of the temperature it was found possible to obtain a product which corresponded to one or other of the well-known types of the naturally occurring oil, and in consequence of their results they have put forward the hypothesis that much of the world's supply of petroleum is due to the action of hydrocarbons on finely divided metals, which they assume to be present in the earth's interior.

#### OCCURRENCE OF PETROLEUM

GEOLOGICAL OCCURRENCE.—The main supply of petroleum is derived either from sandstone or from limestone rocks. Furthermore, it generally occurs in anticlines and synclines, and it is to be supposed that, owing to the pressure of the gas and water which always accompany an oil deposit, the petroleum is forced to the surface when any vent is provided. In almost all oil deposits rock salt is also found, and this fact has hitherto remained unexplained. It may be, however, that the fact that access of water has been prevented is in some way connected with the non-escape of the oil. In each case this would be achieved by the presence of an impervious covering.

SOURCES.—The principal sources of petroleum are the following. The United States, where it occurs chiefly in rocks of Carboniferous, Devonian, and Silurian age; in Russia, in rocks ranging from the Cretaceous to the Miocene; and in Galicia and the Balkan states, where it is chiefly found in the Tertiary deposits. In addition to these places there are a number of others where in recent years huge stores have been discovered, and these promise to take the place of the older and better-known ones when the latter shall have become more or less exhausted. Amongst these mention must be made of Assam and Burma, Northern Africa, the Eastern Archipelago and Japan, and certain districts in South America.

OIL SHALES.—Besides these spots where the oil is already formed, there are others where the rocks yield on distillation a product closely allied to the ordinary petroleum. The carboniferous shales of the Lothians in Scotland are extremely productive, and in various places in Europe, Africa, and America similar shales occur, which are now worked or will be worked within the near future.



**KINDS**—Broadly speaking, petroleum may be divided into three classes: the American, the Caucasian, and the Galician types. These differ in their properties, since they are mixtures of hydrocarbons belonging to different series. For example, the AMERICAN OIL is mainly composed of hydrocarbons of the paraffin series, having the general formula  $C_nH_{2n+2}$ , and ranging from pentane,  $C_5H_{12}$ , up to  $C_{30}H_{62}$ ; while the Russian or CAUCASIAN OIL is made up chiefly of the naphthenes  $C_nH_{2n}$ , together with a great variety of hydrogen derivatives of the aromatic series. The GALICIAN OIL, on the other hand, may be described as being intermediate in composition between the other two.

**SHALE OIL**.—The oil obtained by the distillation of the oil-bearing shales is chiefly remarkable in that it contains exceptionally large quantities of the solid hydrocarbons.

**CRUDE PETROLEUM** varies much in appearance. Some is dark and viscid, while other kinds are mobile and of a pale straw colour. The specific gravity is generally between 0.8 and 0.9, and, speaking generally, the lighter the oil the better for illuminating purposes, while the heavier kinds are more suitable for fuel.

**DISTILLATION PRODUCTS**.—The crude oil is subjected to the process of distillation, and the following products are usually isolated from the different fractions:—

Name	Specific Gravity.	Boiling-point.
Petroleum ether ... ..	0.665 to 0.67	50° to 60°
Benzoline ... ..	0.68 to 0.72	70° to 90°
Ligroin ... ..	0.73 to 0.77	90° to 120°
Kerosene ... ..	0.78 to 0.82	150° to 300°
Lubricating oils		
Vaseline } ... ..		
Paraffin wax }		

The various products are further purified, in some cases by another distillation, in others by a process of washing successively with sulphuric acid and caustic soda, this latter method being applied to the petroleum oil for burning. The heavier fractions containing the lubricating oils are cooled to a low temperature, so that the solid paraffin separates. The adhering oils are removed by treatment in hydraulic presses.

**LAMP OIL**.—For burning in lamps it is important that the oil should be such that no inflammable vapour is given off at the temperature to which the oil is raised in the process of burning. This is expressed in technical language by saying that the oil must have a FLASH-POINT above a certain fixed standard. This standard is, in the United King-

dom, 73° F., and all oils are tested by means of the Abel flash-point apparatus.

VASELINE.—Of the other products obtained in the distillation of crude petroleum mention must be made of VASELINE, the residue from the American oil. This is concentrated to a thick, buttery consistency and then dissolved in petroleum ether, the solution repeatedly treated with animal charcoal to decolorize it, and then heated so as to remove the solvent.

OZOKERITE is a naturally occurring wax found in large deposits in Galicia and Roumania. It is composed mainly of the higher paraffins, and is subjected to refinement before being used for the manufacture of candles and other commodities.

### SCOTTISH SHALE OIL

PREPARATION AND DISTILLATION OF SHALE.—The oil-bearing shales are mined and broken into small pieces about 6 in. square. These are placed in vertical retorts, which are generally about 30 ft. in height and take a charge of 1½ ton. The heating is so conducted that the lower portion of the retort is raised to a bright-red heat while the upper portion is only dull red. The process is continuous, and as spent shale is withdrawn from the base a fresh supply is introduced through the hopper at the top of the retort. The products of the distillation are passed through a series of condensers and the distillate separated into an ammoniacal and an oily layer.

The yield from the shales distilled in Scotland is about 20 or 30 gallons of oil per ton, and in addition some 60 or 70 lb. of ammonium sulphate are obtained.

The ammoniacal liquor is distilled and the ammonia passed into sulphuric acid. The ammonium sulphate thus formed is one of the by-products which enable the shale-oil industry to compete against the foreign oils that are to-day so largely imported.

REFINING.—The refining of the crude shale oil is carried out in much the same fashion as in the case of the crude petroleum. Steam is blown into the stills and three main fractions are separated, namely, light oils, heavy oils, and paraffin wax. The light oil yields naphtha and burning petroleum, while the heavy oils are worked up for lubricating oils after the paraffin has been separated by cooling and pressing.

The impure paraffin is purified by what is known as *sweating*. It is melted and pumped into perforated trays floated upon a layer of cold



water. When the wax has solidified, the water is drawn off and the cake of paraffin slowly heated in stoves. The temperature is raised so slowly that only a portion of the wax melts and drains away, carrying with it most of the impurities. The residue is again melted, treated with animal charcoal, and then moulded into cakes. These are largely used in the manufacture of candles.

The distillation of other oil shales is carried out in a similar way to the one just described, though, on account of the differences existing in the original composition of the shale, the products differ not only in kind but also in quantity.

Before leaving the subject of petroleum reference must be made to the vast development that has taken place in this industry as a result of the introduction of the INTERNAL-COMBUSTION ENGINE. For this purpose the lighter fractions of the petroleum are generally used, though for certain types of engines "petrol" is not essential. Crude petroleum is also used largely as a fuel.

#### THE PREPARATION OF IMITATION PRECIOUS STONES

**PASTE.**—The most common of the imitations of the well-known precious stones are generally referred to as PASTE. The basis of all these imitations is a dense, readily fusible glass known as "strass". This consists of a glass containing a considerable proportion of lead oxide, and in addition potash, with smaller amounts of borax and arsenious oxide. The various colours are obtained by the admixture of different metallic oxides. For example, the imitation ruby is prepared by adding to such a paste a suitable amount of manganese dioxide; the amethyst is coloured by the addition of a mixture of manganese and cobalt compounds; emerald is imitated by the addition of copper salts, to which is also added a certain amount of antimony oxide.

**IMITATION GEMS.**—A distinction is to be drawn between the paste stones and the imitation ones. These latter are obtained usually by means of the electric furnace. In some instances larger stones have been prepared by fusing in the electric furnace a number of smaller genuine stones. On the other hand, by fusing alumina and adding the requisite quantity of coloured oxides, such as chromium oxide, it has been found possible to prepare crystals which are very passable imitations of the real articles. In this way artificial rubies and sapphires have been prepared.

**ARTIFICIAL DIAMONDS.**—Reference will be made to the manufacture of artificial diamonds by the method devised by the late M. Henri

Moissan, and it is quite possible that in the future his method may be further developed so as to render possible the preparation of gems other than those at present made by artificial means.

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## CHAPTER VIII

### THE APPLICATION OF ELECTRICAL METHODS TO CHEMICAL INDUSTRY

There are probably no branches of chemical industry that have made such progress as those in which it has been found possible to apply electrical methods. In the extraction of metals from their ores, in the refining of crude metals, in the manufacture of substances of commercial importance, and in the preparation of countless articles in daily use, processes involving the use of electric power have been found to be of the greatest importance. A few years ago sodium and aluminium were, comparatively speaking, rare substances; to-day they are both produced in enormous quantities by electrical means. The introduction of the ELECTRIC FURNACE has made possible the preparation of many compounds the existence of which was not even suspected, and has revolutionized the manufacture of substances previously obtained only by chemical methods. It must not be supposed, however, that there is any particular magic in these new processes. Generally speaking they are only alternative methods, and their employment is decided solely by the cost of working. Where there is abundant water power, and where fuel is cheap, the choice between an electrical and a chemical process would probably rest with the former, provided, of course, that other things were equal. In the following pages a summary will be given of the chief processes in which electric power is employed.

#### WINNING OF METALS FROM THEIR ORES

In the case of some metals it has been found possible to extract the metal directly, while in other cases it has so far only proved practicable to employ electrical methods for the refining of the crude product obtained by chemical means. Aluminium and sodium are at present prepared almost exclusively by electrolytic processes, and it will be well to consider first the methods by which they are obtained.

**ALUMINIUM.**—It is impossible to prepare aluminium by the reduction



of the oxide with carbon, as can be done in the case of the allied metal iron. Even at the high temperature of the electric arc, a mixture of alumina and carbon yields no aluminium but a carbide,  $\text{Al}_4\text{C}_3$ , and the chemical method by which the metal was formerly produced depended upon the reduction of the chloride by sodium. This process was exceedingly costly, even after the introduction of Castner's method of obtaining sodium by reducing a mixture of caustic soda with a mixture of iron and carbon, and prevented use on a commercial scale. Now, however, aluminium can be produced at 1s. per pound, and about 20,000 tons are made annually by electrolytic processes.

**HÉROULT PROCESS.**—The main supply of aluminium is derived from the electrolysis of alumina by what is known as the Héroult process. Other processes are in use, but they are all similar in type to the one described below. The Héroult process is at present worked by the British Aluminium Company at Foyers, in Scotland, and by the Aluminium-Industrie-Aktien-Gesellschaft at Neuhausen, Switzerland. The principle of the method is as follows: Pure alumina, dissolved in cryolite or in a mixture of a similar nature, is kept in a state of fusion by the heat generated by the passage of an electric current which at the same time decomposes the electrolyte, giving aluminium at the cathode and oxygen at the anode.

**ADVANTAGES OF ELECTRICITY.**—It might be thought that to use for the purpose of heating, such a costly form of energy as the electric current is unnecessary extravagance, but on closer enquiry it will be seen that this waste is more than counterbalanced by the saving in other ways. If external heating were employed, the walls of the vessel in which the fusion took place would, unless they were made of platinum, suffer enormously in consequence of the high temperatures, and so continually need renewal. In the second place, the heating by the current prevents waste of energy by diffusion, since there is no chance of loss, as the energy is applied where needed, namely, in the centre of the mass, so that it is possible to keep a thick layer of solid alumina lining the vessel, thus preventing loss of heat and the destruction of the walls.

**MANUFACTURE OF ALUMINIUM.**—The essential parts of the apparatus used are shown in fig. 69. The vessel A is made of iron and is lined with plates of carbon B. For the preparation of pure aluminium the cathode E is made of aluminium, but as the process was originally devised for the manufacture of a copper-aluminium alloy, the cathode is often of copper. The anode H is formed of good electrode carbon, and projects into the cavity of the cell D. In the cover of the cell are two holes G G

through which the electrolyte (alumina) and, if necessary, copper can be fed. At the bottom of the cell is a tapping hole F, closed by a rod in the form of a screw. Through this tapping hole the metal C is drawn off when a sufficient amount has accumulated.

The first step in the manufacture of aluminium is the preparation of pure alumina from bauxite. This is absolutely essential if a metal of good quality is to be obtained. The bauxite is first crushed, and then roasted in a revolving furnace at such a temperature that all the iron is converted into ferric oxide. The roasted mass is then crushed to a

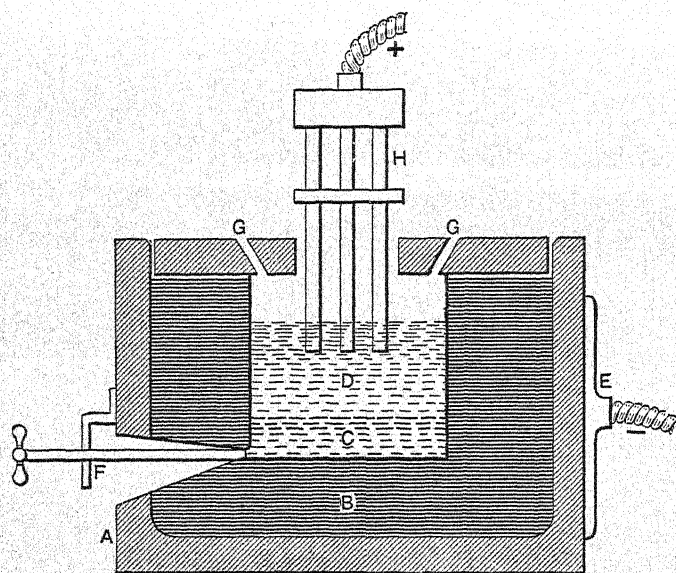


Fig. 69.—Diagrammatic Representation of the Furnace used in the Héroult Process

moderately fine powder and treated with a strong solution of caustic soda. After a few hours this solution is diluted and filtered. The sodium aluminate was formerly decomposed by a current of carbon dioxide, but, as this was somewhat expensive, another method has been devised. This is known as Bayer's method, and consists in treating the solution with a small amount of alumina obtained in a previous operation. By this means the solution, in the course of a few hours, deposits about 70 per cent of its alumina. The precipitate is separated, washed, and dried at about  $1100^{\circ}\text{C}$ . In this way the alumina is rendered insoluble, and no longer possesses the property of taking up water. The caustic soda solution, from which most of the alumina has been separated, is concentrated and used for treating a further quantity of bauxite.

The operation is begun by placing aluminium (or copper) in the



furnace and lowering the anode until it touches the metal. When the current passes, the metal fuses, and the anode is gradually raised, while pure alumina and cryolite are fed into the cell through the holes in the cover. As this process is worked there is little or no decomposition of the cryolite, which merely serves as a solvent for the electrolyte.

**SODIUM.**—Sodium was first prepared by Sir Humphry Davy. He obtained it by the electrolysis of fused caustic soda, a process which is now used on a commercial scale for the preparation of practically all the sodium which is used. The electrolytic method in use at present is one devised by Castner, who had previously greatly improved the manufacture

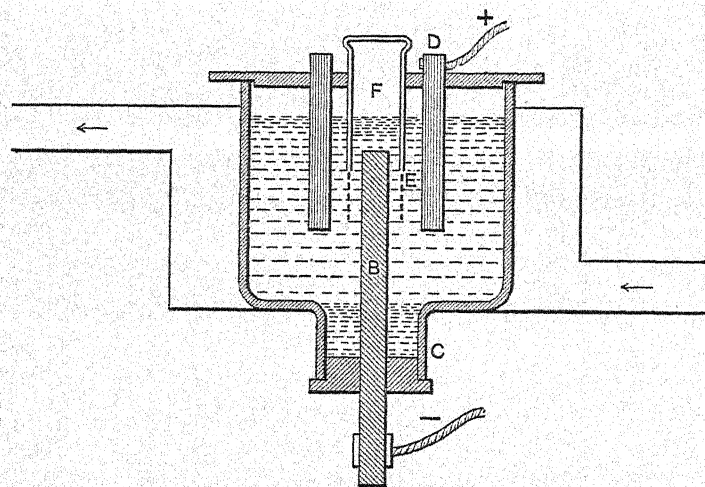


Fig. 70.—Diagram illustrating the Castner Apparatus for the Manufacture of Sodium

by chemical methods. The reaction is an exceedingly simple one, as sodium and hydrogen are liberated at the cathode, while oxygen is set free at the anode.

In practice a bottle-shaped cell is used, which is heated to a temperature just sufficient to fuse the caustic soda. The neck of the cell C is not heated, so that the caustic soda solidifies there, and serves to make the joint between the cathode and the wall of the containing vessel. The arrangement of a Castner apparatus is seen in the accompanying figure (fig. 70). The iron cathode B projects upwards into the cell, and is surmounted by a cylindrical vessel F in which the sodium collects. Hanging from this cover is a wire-gauze cylinder E which allows the electrolyte to have free access to the cathode, but prevents the fused metal from passing into the body of the cell. The anode D, which is frequently of cylindrical form, surrounds the upper portion of the cathode, and is

perforated so as not to impede the passage of the electrolyte. During electrolysis the sodium collects in the vessel, where it is of course surrounded by an atmosphere of hydrogen, which prevents it from any great amount of oxidation. The metal is removed at frequent intervals, and, provided this is done, and the temperature not allowed to rise much above the melting-point of the caustic soda, the process works very smoothly and yields a product of good quality.

**MAGNESIUM.**—Magnesium was formerly made by the reduction of the chloride with sodium and subsequent distillation, but at the present time it is prepared electrolytically from carnallite,  $\text{KClMgCl}_2 \cdot 6\text{H}_2\text{O}$ .

The process is carried out in an iron vessel which serves as the cathode. The cell is covered by a lid, through which passes the carbon anode surrounded by a porcelain cylinder. As magnesium is an easily oxidizable metal it is necessary to take precautions to prevent the access of oxygen. This is usually effected by leading into the cell nitrogen or some other inert gas. The magnesium collects on the surface of the fused carnallite, and the chlorine liberated at the anode escapes through a pipe leading from the porcelain cylinder.

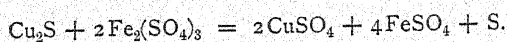
One difficulty that has been experienced is that the metal as it is set free collects in the form of globules, which are prevented from running together by the formation of a film of magnesium oxide on their surface. This difficulty has been overcome to some extent by adding a small amount of calcium fluoride to the electrolyte.

**COPPER.**—Commercially the winning of copper from its ores is not successful. In spite of this fact at least two processes have been attempted on a manufacturing scale. These are the Siemens-Halske and the Hoepfner processes, and, although at present they are scarcely satisfactory from the investor's point of view, there is yet considerable hope of ultimate success.

**OLD PROCESS.**—In the ordinary method of copper smelting a product known as coarse metal is obtained. This has approximately the composition represented by the formula  $\text{Cu}_2\text{SFe}_2\text{S}_3$ . Originally this substance was used as the starting-point for the preparation of copper by electrolytic means. The coarse metal was made the anode in a cell, and a sheet of pure copper the cathode upon which the metal was deposited. The method was not a success, as the anode was dissolved unevenly, and became coated with a layer of sulphur. Later, "white metal", a further stage in the ordinary manufacture of copper, was used as the anode, but the same objection was found to its use; so both these methods were finally abandoned in favour of one of the two following processes.



THE SIEMENS-HALSKE METHOD.—The principal ore employed is copper pyrites, which has the approximate composition  $\text{Cu}_2\text{SFe}_2\text{S}_3$ . This is roasted in revolving furnaces, and during the process the sulphur is converted into sulphur dioxide (which is used for making sulphuric acid), the iron into ferric oxide, and the copper sulphide is partially oxidized to copper sulphate. The roasted ore is treated with sulphuric acid, whereby any copper sulphate present is dissolved, while the oxide of iron is converted into ferric sulphate, which dissolves the unchanged cuprous sulphide. This process of extraction, or *leaching* as it is called, is so conducted that the fresh liquor comes in contact with ore that has been nearly exhausted by previous leaching, while fresh ore is treated with a solution that is almost saturated. The equation representing the change is—



The solution of ferrous sulphate and copper sulphate is then electrolysed in a cell in which the anodes are of carbon and the cathodes sheets of pure copper.

The cell is so arranged that the anode and cathode compartments are separated by means of a diaphragm. During electrolysis the copper is deposited on the cathode, while the ferrous sulphate in the anode compartment is oxidized to ferric sulphate. The ferric sulphate so obtained is used for the extraction of a fresh quantity of ore.

THE HOEPFNER PROCESS.—The finely crushed ore is extracted with a strong solution of cupric chloride and calcium chloride. This is carried out in revolving wooden drums, into which steam is blown for the purpose of heating. An excess of cupric chloride is employed, since it reacts with the pyrites to form ferrous chloride and cuprous chloride, the former acting upon more cupric chloride to give ferric chloride and cuprous chloride. The solution thus obtained is electrolysed in a cell in which the anode and cathode compartments are again separated by means of a porous diaphragm. The cells are so arranged that the solution flows from one to another, the copper being deposited on the cathodes, while chlorine is set free at the anode. The chlorine disengaged acts upon the unaltered cuprous chloride, giving cupric chloride, which is used for the extraction of fresh ore. One respect in which this process differs from the Siemens-Halske is, that the anodes are of carbon coated with paraffin, and the anode and cathode compartments are separated by a diaphragm made of parchment paper.

Although so far it has not been found highly profitable to extract copper from its ores by electrolytic methods, yet in the refinement of

crude metal the introduction of electrical processes has entirely revolutionized the copper industry. An account of this refining will be given in a later section.

**GOLD.**—Gold usually occurs in the native form, and is freed from extraneous matter by the extraction of various solvents, of which a very weak solution of potassium cyanide is the most common. Formerly the gold was thrown out of solution by the addition of metallic zinc, but at the present time there is a tendency to replace this method of precipitation by electrolytic methods.

The **SIEMENS-HALSKE PROCESS** is a very simple one, and consists in electrolysing the cyanide solution between iron anodes and lead cathodes. The chief expense in working is the replacing of the electrodes, as the iron anodes are disintegrated by the cyanide forming Prussian blue, while the lead cathodes have to be removed from time to time in order to separate the gold.

**SILVER.**—From argentiferous ores silver is still extracted by one or other of the old methods, but for purposes of separation of silver from gold the employment of electrical methods has been of great advantage.

**SEPARATION OF GOLD AND SILVER.**—Gold as obtained from its ores frequently contains a considerable amount of silver. The separation of the two metals was at one time effected by fusing the alloy with as much silver as was necessary to lower the percentage of gold to about thirty. Such an alloy is attacked by nitric acid, whereby the silver is dissolved while the gold is left.

The objection to this method is that a considerable amount of acid is wasted. If, however, an alloy containing about 75 per cent of silver and 25 per cent of gold is made the anode of an electrolytic cell with nitric acid as electrolyte, the silver is deposited on the cathode and the gold left in the form of a sludge. The operation is exceedingly simple. The cathode is a thin sheet of pure silver, and the metal is deposited thereon in the form of crystals. To prevent the gold sludge from mixing with the silver the anodes are wrapped in filter cloth. The cathodes are brushed from time to time, and the silver crystals collected on a tray which rests on the bottom of the vat.

**ANTIMONY.**—The chief ore of antimony is the sulphide,  $\text{Sb}_2\text{S}_3$ . This is treated with a solution of sodium sulphide, in which the ore dissolves. The solution so obtained is electrolysed in cells divided into anode and cathode compartments by means of a porous diaphragm. In the anode compartments is a solution of common salt. Antimony is deposited on the iron cathodes, and chlorine is set free at the carbon anodes. As



obtained in this way, the metal is almost as pure as that made by the ordinary smelting process. It contains on an average about 99.7 per cent of antimony.

**ZINC.**—Zinc is a metal which theoretically should be easily obtained from its ores. As a matter of fact, the winning of it electrolytically is attended with considerable difficulty. The main obstacles to be overcome are these. Firstly, when solutions containing zinc are electrolysed there is always a tendency for the zinc to be deposited in a spongy form; and secondly, unless certain precautions are observed hydrogen is disengaged. Broadly speaking, there are three main directions in which attempts have been made to win zinc electrolytically. These are:—

- I. Electrolysis of a solution of zinc sulphate.
- II. Electrolysis of a solution of zinc chloride.
- III. Electrolysis of fused zinc chloride.

It is obviously important that energy should not be wasted in liberating hydrogen instead of the metal. This end is attained by keeping the solution fairly strong, and by avoiding too great an excess of acid. To avoid the deposition of spongy zinc it is important that a high-current density should be used. If these conditions are fulfilled, it would seem practicable to win zinc more economically by electrolytic means than by the older methods.

**SIEMENS-HALSKE AND ASHCROFT PROCESSES.**—The first method has been attempted on a manufacturing scale in at least two modifications. These are the Siemens-Halske and the Ashcroft. In both, the principles are similar. The ore is crushed and roasted in such a way that the sulphides are converted into sulphates and not into oxides. This is a matter of considerable difficulty, and the expense forms no small part of the total cost of working. The roasted ore is then extracted with dilute sulphuric acid. Any lead which may be present is converted into insoluble lead sulphate, and at the same time zinc and other metals pass into solution as sulphates. Careful purification of the solution follows, since without this the quality of the product is impaired. The purified solution is then electrolysed between lead anodes and thin zinc cathodes.

Various modifications of the second method are employed. In one the ore is first roasted, and then again roasted with common salt to convert the zinc into chloride. The mass is lixiviated and the solution cooled, in order that sodium sulphate may be deposited. The zinc chloride solution is then electrolysed in cells provided with a diaphragm. Chlorine appears at the anode, and is used for making either bleaching powder or chlorates.

In another process the roasted ore is treated with a solution of calcium chloride, and carbon dioxide is passed into the mixture. Zinc chloride dissolves, and the calcium is removed as carbonate. The solution of zinc chloride is then electrolysed as in the other process.

For the electrolysis of fused zinc chloride an apparatus similar to the one used in the preparation of aluminium is employed. The anodes are of carbon and the cathode is fused zinc.

MOISSAN'S RESEARCHES.—In the course of his remarkable researches, connected with the use of the electric furnace, Moissan has shown that a large number of metals may be prepared by reduction of their oxides with carbon. Aluminium, barium, calcium, chromium, manganese, molybdenum, strontium, tungsten, uranium, and vanadium have all been prepared in this way, and it is extremely probable that in the near future the preparation of metals like tungsten and chromium will be carried out on a large scale, because of their importance in the manufacture of certain steels having special properties.

#### THE ELECTROLYTIC REFINING OF METALS

In certain instances the refining of metals by electrolytic methods has been singularly successful. This is notably the case in the copper industry, in which the process of refining has so much improved that at the end of the first ten years during which the process was tried the output was ten times as great as at the beginning. In addition to this increase it must be noted that comparatively enormous quantities of gold and silver were recovered in process of refining.

COPPER.—Copper as it comes to the hand of the refiner usually contains about 2 per cent of impurities. Of this 0.3 may be silver and 0.001 gold. The remainder is made up chiefly of oxygen, arsenic, and antimony.

The principle of refining is very simple. The crude metal is made the anode in an electrolytic cell in which an acidified solution of copper sulphate is the electrolyte, and thin sheets of pure copper form the cathode. Pure copper is deposited on the cathode, and the impurities fall to the bottom of the cell in the form of a sludge. Working details differ in the various refineries, but the same principles apply throughout.

As a general rule, the crude metal is cast into bars about 36 in. long, 18 in. wide, and  $\frac{3}{4}$  in. thick. The cathodes are of similar shape, but much thinner, usually only about  $\frac{1}{8}$  in. thick. A number of vats are employed, and the anodes and cathodes are so arranged that each forms one main



electrode. The anodes and cathodes are arranged alternately at a distance of 2 in. from each other. There are various devices for securing a uniform flow of electrolyte. In some cases compressed air is used to force the copper sulphate through the vats; in others, the vats are arranged one below the other in terrace fashion, so that the fluid circulates by gravity, and is pumped from the lowest to the highest. It should be noted that these are only minor details, and, however much they differ from each other, the main principles involved are the same in all cases. The resulting metal is of great homogeneity and of a high degree of purity.

NICKEL.—For many years the art of nickel plating has been practised, but it is only comparatively recently that it has been possible to prepare nickel plates of any appreciable thickness. It has long been known that if, in the course of plating, the process was allowed to proceed for any length of time, instead of obtaining a thick plate of the metal, the thin film curled up and detached itself from the object on which it was being deposited. Now, however, nickel is deposited in fairly thick sheets, though the method by which this result is attained is kept as a secret. It is more than probable that the process is somewhat of the following nature. The electrolyte is a solution of nickel sulphate, and the electrodes are both of nickel. The current density employed is fairly high, and the electrolysis is conducted at a moderately high temperature.

SILVER.—The electrolytic refining of silver is practised to a large extent in the United States of America. The process adopted is essentially the same as the one described for the parting of gold and silver, and calls for no further comment.

There are certain other metals which are refined to a small extent electrolytically; but, as in most cases the ordinary processes are equally satisfactory, it is scarcely necessary to describe them here. Probably in the space of a few years there will be great developments in this and other branches of electrochemistry. Wherever power can be obtained at a low cost the choice between an electrolytic and a non-electrolytic method will, other things being equal, rest with the former, as it allows such wide scope for refinements in detail, and therefore renders possible the production of a great variety of substances of different grades.

#### THE ELECTRIC FURNACE

COWLES' FURNACE.—The first attempt to employ the electric current for purposes of producing high temperatures on a manufacturing scale was that of the brothers Cowles. They designed a furnace for the pro-

duction of aluminium alloys and for the reduction of zinc ores. Commercially, neither of these methods has been successful; but the fact remains that by their attempts they laid the foundation of a highly important industry.

**MOISSAN'S FURNACE.**—In the course of his researches on the production of artificial diamonds, Moissan gradually perfected the form of electric furnace that is universally used to-day. Essentially the furnace consists of blocks of lime hollowed out in such a way that a cavity is formed. Into this cavity carbon electrodes project, and on passage of a current an enormously high temperature is reached, rendering possible reactions which were hitherto impossible. A diagrammatic representation of such a furnace is given in fig. 71.

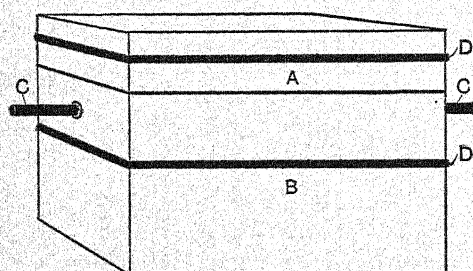


Fig. 71.—Diagram illustrating an Electric Furnace

A, Cover. B, Body of furnace. CC, Electrodes. DD, Iron bands to strengthen furnace

Moissan succeeded in obtaining not only artificial diamonds, but a great variety of compounds previously unknown. A short account of some of these will be given below.

#### ARTIFICIAL DIAMONDS.—

The method adopted by Moissan for the preparation of diamonds was briefly as follows. Iron

saturated with carbon at a high temperature was suddenly cooled in such a way that the outer crust became solid almost instantaneously, thus producing an enormous pressure in the interior of the mass. After this first sudden chilling the cooling was allowed to proceed very slowly, and during this process the dissolved carbon was gradually thrown out of solution and assumed the crystalline form.

In this way Moissan succeeded in obtaining true diamonds, microscopic in size, it is true, but nevertheless perfect in crystalline form and showing all the properties of those found in nature.

Moissan's attempts in this direction have been followed by others, notably those of Sir William Crookes. In these latter experiments a high pressure and a high temperature were simultaneously produced by explosions in steel cylinders. The resulting diamonds were of the same kind as those obtained by Moissan.

After the success which crowned his first attempts, Moissan made further experiments in other directions. In a remarkable series of researches he has shown the great possibilities of the electric furnace. By



means of it temperatures deemed unattainable have been reached. At a lecture given before the Royal Institution in 1906, Moissan showed some experiments which served to illustrate the application of the furnace to work in which high temperatures are required.

**CARBIDES.**—From an industrial point of view the preparation of CARBIDES is probably the most important result yet achieved. The first carbide to be prepared was that of calcium. Wohler, in 1862, prepared this compound in an impure form, but it was first obtained in a state of purity by Moissan in 1892. Using an electric furnace, of which the body was made of lime and the electrodes of carbon, he found that calcium carbide was formed. This body, at a temperature of about  $3000^{\circ}\text{C}$ ., was liquid and could be run off from the furnace. On cooling, it solidified to a dark-coloured mass of crystalline structure.

In practice the furnace is not made of lime but of firebrick, and into it is fed a mixture of lime and coke. In the original type of furnace the firebrick was lined with carbon, and the crucible so formed constituted one electrode. The other was a stout carbon rod which was gradually raised as the current passed. In this form of furnace there is a considerable loss of energy by diffusion of heat, and the walls of the crucible undergo corrosion. Attempts have been made to remedy this defect, and in the more modern type of furnace these objections no longer obtain.

**SILICON CARBIDE.**—This carbide, known commercially as CARBORUNDUM, was discovered by Acheson, and is at the present time manufactured principally at his works in Canada. The furnace is of firebrick, and is charged with a mixture of coke, sand, sawdust, and a small amount of common salt.

The chief use of carborundum is as a substitute for emery. When taken from the furnace the solid mass is broken, ground to a fine state of division, and washed, first with water and then with acid. It is made into grinding wheels, and into paper and cloth similar to the well-known emery products.

**OTHER CARBIDES.**—Many other carbides have been prepared, but at present they are of no more than theoretical interest. Barium, lithium, and strontium form carbides of the same type as calcium. That is to say, on treatment with water acetylene is evolved and the hydroxide of the metal is left. Aluminium carbide has the composition  $\text{Al}_4\text{C}_3$ . It forms yellow crystals which with water give methane. Manganese carbide,  $\text{Mn}_3\text{C}$ , similarly treated, gives a mixture of methane and hydrogen. Uranium carbide,  $\text{UC}$ , yields a complex mixture of methane, ethylene, hydrogen, and certain solid and liquid hydrocarbons. Boron and titanium

carbides are exceedingly hard substances—so hard, in fact, that they will cut diamond, and it is possible that in the future they may be used to a limited extent for this purpose. Various carbides of iron are known, and to the preponderance of one or other of these the different kinds of steel probably owe their distinctive properties.

**SILICIDES.**—A few of this interesting class of compounds are used commercially, principally those of iron and copper.

**COPPER SILICIDE** has the formula  $\text{CuSi}$ . It is employed to add to copper for the manufacture of wire used in electrical work. The silicon apparently exerts a reducing action, and leaves a metal of high conductivity. A silicide of iron of the composition  $\text{FeSi}$  is known, but up to the present has found no commercial application. What is probably a mixture of various silicides of iron is used under the name of ferrosilicon. It is prepared by heating a mixture of coke, sand, and ferric oxide in a furnace similar in type to the one used in the manufacture of calcium carbide.

The silicides of the metals of the alkaline earths have been obtained by heating a mixture of the oxide, silica, and coke. They are white, crystalline bodies which react with water, giving silica and hydrogen.

**BORIDES.**—Moissan has prepared several borides, but so far none of them has found any industrial application. **CARBON BORIDE** is perhaps the most interesting, as, next to diamond, it is the hardest known substance. It has the formula  $\text{CB}$ , and may be crystallized from fused copper.

### ELECTROPLATING

The process of covering an inferior metal with a more durable or costly one has been in use for many years. Formerly this was done by rolling together plates of the two metals, but of late years this method has given place to one in which a layer of the desired metal is deposited by means of the electric current. It is this process that is known by the name of electroplating.

The metals usually so deposited are gold, silver, copper, and nickel.

**GOLD PLATING.**—The articles to be gilded are first thoroughly cleaned by immersion in a bath of caustic soda, from which they are well rinsed. They are then dipped in acid (usually nitric acid) and again washed. Finally they are generally subjected to a process known as "quicking". This is merely a momentary immersion in a dilute solution of a mercury salt. A thin film of mercury is formed upon the surface, to which gold will adhere.

The electrolyte is a solution of the double cyanide of gold and



potassium, and contains about 10 per cent of cyanide and 1 per cent of gold. The articles are made the cathode and a plate of pure gold forms the anode. The colour of the deposit may be modified by using some alloy instead of pure gold. If, for example, one of gold and silver is used, the resulting layer is lighter in colour, while if copper is substituted for silver, the deposit is of a much deeper shade.

**SILVER PLATING.**—The process of silver plating is very similar in character to the one last described. The silvering solution, as before, consists of the double cyanide, and varies in strength according to the character of deposit required. There are many details which have to be observed in practice in order to secure the best results, but for these a work on electro-deposition of metals must be consulted. One interesting fact may be mentioned with reference to the possibility of obtaining a bright deposit. As a rule the film of silver deposited in the ordinary process of plating is dull, and requires burnishing by mechanical means. If, however, a trace of carbon bisulphide is added to the electrolyte, the silver, instead of having a mat surface, is perfectly bright.

**NICKEL PLATING.**—Nickel has many advantages over silver as a coating for easily oxidizable metals. It is harder, tarnishes less readily, and is much cheaper. Against these must be set the objections that the colour is not so pleasing, and also that the actual deposition is far more difficult than in the case of silver. At the present time the electro-deposition of nickel is carried out on a large scale, and by careful attention to details excellent deposits may be obtained.

Great care must be employed in the preparation of the articles before they receive their coating of metal. The surface must be perfectly clean and smooth, or the nickel will peel away. Generally speaking, no more than a thin film is deposited, as the thinner the film the greater is the likelihood of its adhering. A solution of nickel ammonium sulphate is used as the electrolyte, and the anodes are of nickel, which should be as pure as it is possible to obtain it.

**COPPER PLATING.**—The deposition of copper as a covering is not practised to any great extent, but for the making of copies of articles in relief the process of **ELECTROTYPING** is widely used. A mould of the article to be copied is made in fusible metal, gutta percha, plaster of Paris, or some other medium. This is coated with a thin film of graphite or other conducting substance, and made the cathode in an electrolytic cell. The electrolyte is an acidified solution of copper sulphate, while the anodes are of the purest electrolytic copper.

Copper is sometimes deposited on iron to prevent it from corroding.

This is best done in an alkaline bath containing the double cyanide of copper and potassium, with a little ammonia. Instead of this solution a bath made of copper sulphate, Rochelle salt, and caustic soda may be used. The tartrate prevents the precipitation of cupric hydroxide, and from the solution an even deposit of copper is formed. In cases where iron or steel is to be coated with nickel it is frequently found advisable first to deposit a thin layer of copper, as the nickel adheres much more firmly to this than to the iron.

**ZINC PLATING.**—Of other metals which are deposited electrolytically mention need only be made of the cases of zinc and iron. The former metal is used very largely as a protective covering for iron and steel. Formerly a process known as GALVANIZING was extensively employed. This consisted in immersing the iron in a bath of molten zinc. A superficial alloy of zinc and iron was thus formed which constituted a fairly-efficient covering. This process is still largely used, but for certain articles a newer and in many ways more advantageous method is now applied. This is the electrolytic deposition of zinc from a solution of zinc sulphate. A carbon or other insoluble anode is used, and the bath is replenished by the addition of zinc oxide to neutralize the sulphuric acid set free during electrolysis. The method would seem to be in the long run more economical than the older process, and it is probably only a question of time before it is more generally adopted.

**IRON PLATING.**—Iron deposited electrolytically from a solution of ferrous ammonium sulphate is used for the purpose of covering electrotypes of soft metal. When so deposited, iron is exceedingly hard, and so valuable for this particular object. According to some authorities the hardness is due to the presence of a considerable amount of hydrogen, but this point is not yet definitely settled.

A process has been devised for the preparation of pure iron by electrolytic methods, but whether this will be commercially successful or not remains to be seen.

Should occasion arise, almost any metal could be deposited in similar ways, but so far there is no demand, and in consequence little is known concerning the conditions under which these processes can be carried out.

#### THE PREPARATION OF CAUSTIC SODA AND CHLORINE

For many years attempts have been made to manufacture alkali by electrolytic methods, either by the decomposition of the fused salt, or by the electrolysis of a solution of sodium chloride. This substance is chosen



not only because it is cheap, but also because chlorine is obtained as a by-product.

**VARIOUS PROCESSES.**—The earliest attempts were those in which the salt was fused and electrolysed between carbon anodes and iron cathodes, but this plan was soon abandoned in favour of others in which the cathode was of lead. The sodium as soon as set free alloyed with the lead, and the alloy could be decomposed with water with the formation of caustic soda. In the VAUTIN METHOD the cathode was fused lead, and in a modification, the HULIN PROCESS, the electrolyte was a mixture of common salt and lead chloride. Other methods similar in type to the above have been tried, but at present the successful manufacture of alkali by electrolytic means is carried out by using a solution of the salt. As an example of these methods the CASTNER-KELLNER PROCESS may be described.

The electrolysis is conducted in a cell a diagrammatic representation of which is given in fig. 72. The cell is

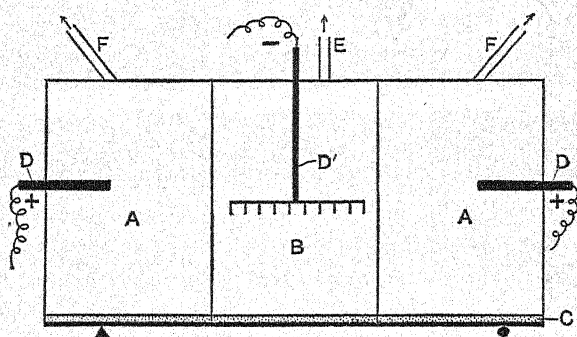


Fig. 72.—Diagram of Castner-Kellner Apparatus for the Manufacture of Caustic Soda

divided into three compartments by partitions which do not reach quite to the bottom of the cell. Where the partitions are, the floor of the cell is hollowed out, and each compartment is separated from the next by a layer of mercury, C, which fills the hollows mentioned, and so makes a tight joint. In the two outer compartments A A salt solution is placed, and in the central one pure water. The centre forms the cathode compartment, while the two outer divisions are the anode compartments. The anodes D are of carbon, and the cathode, D', in the form of a grid, is of iron. Pipes are provided, E F F, for the escape of hydrogen and chlorine respectively. The whole cell rests upon two supports, one of which is a knife edge, and the other an eccentric. This process involves the use of what is known as an intermediate electrode. When a current is passed, sodium is set free at the cathode and chlorine liberated at the anodes. But the mercury acts as cathode to the carbon anodes, and consequently the metal is set free at the surface, where it forms an amalgam. By oscillating the cell, the mercury travels to the cathode compartment, where it becomes the anode to the iron cathode, and so gives up its sodium.

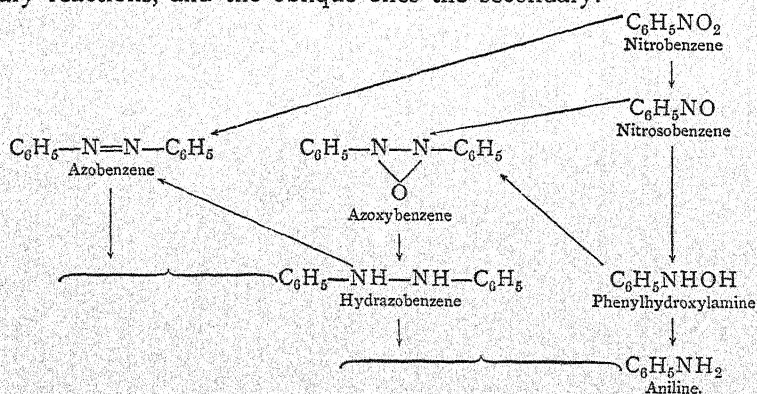
which combines with the water, forming caustic soda. Arrangements are provided for the removal of the caustic soda and the addition of a fresh supply of water and also of brine. Little is known of the actual working details of the process, but it is believed that the salt is first freed from compounds of calcium and magnesium. The evolved chlorine is usually converted into bleaching powder, or in some cases into chlorate.

**HARGREAVES-BIRD PROCESS.**—Another process which has been worked on a manufacturing scale is that known as the Hargreaves-Bird process. In this, sodium carbonate is made by blowing carbon dioxide into the cell, where it combines with the caustic soda formed.

Methods have been devised by which it is possible to produce either hypochlorites or chlorates by the electrolysis of solutions of common salt, but their importance is not sufficiently great to justify a description.

### PREPARATION OF ORGANIC COMPOUNDS

An important branch of the electrochemical industry is that concerned with the preparation of organic compounds. For example, by the electrolytic reduction of nitrobenzene in strong sulphuric acid solution the main product is para amidophenol, but this is formed only as the result of a large number of intermediate reactions. This particular reaction has been studied in great detail, and the result of this study can be summarized in the following scheme prepared by Haber. The vertical arrows show the primary reactions, and the oblique ones the secondary.



As stated, when the electrolysis takes place in strong sulphuric acid solution, the chief product is amidophenol, which is produced by the spontaneous transformation of phenylhydroxylamine; but if it is conducted in acetic acid solution, and a lead cathode be employed, the greater part of the nitrobenzene is converted into aniline.



There are many other substances that can be made electrolytically, such as ortho and para phenylene diamine, iodoform, vanillin, which is the active principle of vanilla, &c. Certain dyestuffs and drugs can also be prepared in a similar way, but at present too little is known of the exact conditions of working to make it possible to say whether these new methods will ultimately replace the existing processes.

### METALS AND METALLURGY

By far the most important developments in metallurgy are those rendered possible by the more general application of electrical processes. These have been dealt with in the section devoted to the application of electricity to industry.

**ALLOYS.**—Great improvements have been made in the preparation of alloys, particularly in the case of steel. Manganese, nickel, and tungsten steels are of the greatest service in modern industry, and useful alloys of aluminium with various other metals are also beginning to play an important part in daily life.

**GOLDSCHMIDT'S CHROMIUM PROCESS.**—An exceedingly important discovery was made by H. Goldschmidt. He found that chromium could easily be prepared by mixing chromium oxide with aluminium powder, and then igniting the mass in a suitable manner. This is accomplished in the following way.

A high temperature "is produced by mixing aluminium powder with barium peroxide, forming a pill of this, and sticking a piece of magnesium ribbon into it. If the magnesium ribbon is ignited, which can be done with a match, the combustion of the aluminium with the oxide of the barium peroxide begins; the mass thereby becomes white hot, and initiates the reaction in the neighbouring portions of the mixture. In proportion as this undergoes transformation, more of the mixture is added, and the temperature thereby soon rises so high that the chromium fuses.

"The method has the advantage that it does not require a specially built furnace, but can be carried out in an ordinary crucible, preferably one of magnesia; the outside of the crucible becomes only slowly warm. On account of the high temperature of fusion of chromium, the preparation of the metal is successful only when large quantities are employed.

"A similar method is used for preparing other metals, and also for the production of very high temperatures. In the latter case cheap oxides, generally iron oxide, are used. With such mixtures fusions, weldings, &c.,

can be carried out on the spot with great ease and certainty, so that the method is of great technical importance."

### THE MANUFACTURE OF STEEL

**BESSEMER PROCESS.**—This is by far the most important method for the making of steel, and consists in blowing through a molten mass of iron a current of air, so that the impurities present are oxidized. The result is a practically pure iron, and to this is added the requisite quantity of an iron containing carbon and other matters.

The operation is conducted in pear-shaped vessels mounted on trunnions. In the first stage the carbon is caused to combine with the iron, and silica is oxidized, so that it forms a slag with the oxides of iron and manganese. In the later stages the carbon is fully oxidized, and carbon dioxide is evolved. The end of this stage is marked by an alteration in the character of the flame, the alteration being observed by means of a spectroscope. The blast is then stopped, and *Spiegeleisen* is added. This is a mixture of steel with manganese and carbon. The carbon added enters into combination with the iron, while the manganese is oxidized and passes into the slag.

**METHOD FOR IRON RICH IN PHOSPHORUS.**—The process as described is only applicable to such specimens of iron as contain a low percentage of phosphorus; but as much of the ordinary pig iron of commerce contains a higher percentage than is compatible with successful working, a method has been devised by means of which it is possible to work with iron containing a considerable amount of phosphorus.

The basis of this method is the fact that if there is present a lining of a basic nature, then the phosphoric acid formed during the oxidation will be taken up by the base. In order to carry out this, the converter is lined with a preparation of dolomite. The limestone is crushed, broken into small pieces, and then strongly heated to remove carbon dioxide and moisture. The heated limestone is then ground to a powder, mixed with tar, and cast into bricks. The converter is lined with these as soon as practicable after their preparation, in order to minimize the chance of their taking up moisture and carbon dioxide.

The lining, after it becomes useless for purposes of absorption, is taken out, and, after grinding, is sold as an artificial manure, its value depending upon the phosphorus which it contains.

**OPEN-HEARTH METHOD.**—A method that is growing in popularity is the open-hearth method. In this the pig iron is melted in an open fur-



nace, with the addition of scrap steel and also of iron ore. The oxygen of the ore combines with the carbon of the pig, and so decarburizes it, leaving a steel.

**CRUCIBLE STEEL.**—Steel of excellent quality is made by melting cemented bars in a graphite crucible. The bars are made by heating pure wrought iron with "cementing powder", which is finely powdered charcoal or soot.

**NICKEL.**—This metal is rapidly increasing in importance. Last year the production amounted to over 10,000 tons, and the bulk of this was obtained from the Sudbury mines in Ontario, U.S.A. The ore is mainly sulphide of nickel and copper. This is roasted so as to oxidize the sulphides to oxides, and the copper removed by leaching with sulphuric acid and crystallization. The residual matter is then reduced with producer gas to the state of metallic nickel, and this is then subjected to the action of a stream of carbon monoxide. A volatile compound known as nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , is thus formed, and this on subsequent heating is decomposed into metallic nickel and carbon monoxide, the latter being again used for the treatment of further quantities of the metal. Various details have to be observed, as, for example, the proper regulation of the temperature and the presence of small granules of nickel, over which the nickel carbonyl has to be passed so as to ensure a proper deposition. The process is comparatively an inexpensive one, as the consumption of fuel is relatively small, and the carbon monoxide necessary is regenerated.

**USES OF NICKEL.**—The chief commercial use for nickel is in the manufacture of alloys. Of these the most important are German silver and the different kinds of nickel steels.

The best GERMAN SILVER has the following composition:—

Nickel	...	...	...	...	...	...	34 per cent.
Copper	...	...	...	...	...	...	46 "
Zinc	...	...	...	...	...	...	20 "

**NICKEL STEELS** are valuable on account of their greater tensile strength and elasticity. They are largely used at the present time for armour plating, and also for the manufacture of heavy guns. The usual alloy approximates to the following composition:—

Nickel	...	...	...	...	...	...	3.00 per cent.
Manganese	...	...	...	...	...	...	0.50 "
Carbon	...	...	...	...	...	...	0.30 "
Iron	..	...	...	...	...	...	96.20 "

## WELDING AND SOLDERING

Within recent years enormous advances have been made in the processes of uniting metals. Mention has already been made of the use of THERMITE, a mixture of aluminium powder and various oxides, but in addition to this there are other important methods in use at the present day.

The OXYHYDROGEN BLOWPIPE was obviously destined to play an important part in work of this description, the great drawback being the high cost of the necessary gases. This objection has been removed by invention of a process, successful on a commercial scale, for the production of oxygen and hydrogen by the electrolysis of water. Since the gases are used in the proportion of 1 part of oxygen to 6 parts of hydrogen, there is a considerable excess of the former, and this forms a most valuable by-product.

Great difficulty was at first experienced in the work of soldering by the oxyhydrogen blowpipe, on account of the formation of a film of oxide on the surfaces of the metal. This has to a large extent been overcome by mixing with the gases a hydrocarbon, such as acetylene, rich in carbon. In this way more carbon dioxide is formed, and it is claimed that the latter is further reduced to carbon monoxide, which itself acts as a reducing agent and helps to remove the film of oxide which would otherwise prevent a proper union of the two surfaces.

For the WELDING OF STEEL PLATES another blowpipe method has been introduced. This is the oxyacetylene method. A mixture of about 1 volume of acetylene with 1.7 volume of oxygen is employed. A very high temperature is attained, and as the sole product of combustion at the place of welding is carbon monoxide, the results are highly satisfactory.

Electric welding plays an important part in the manufacture of RAILS. In principle it is exceedingly simple. The parts to be joined are brought into close proximity and a current passed. At the point of union considerable resistance is set up, and the metal is raised to a high temperature. When the metal is sufficiently soft, pressure is applied at the ends, and the joint so made remains homogeneous on cooling. One great advantage of this method is that different metals, such as copper and iron, can be joined together.

SOLDERING as opposed to welding consists in the joining together of two metallic surfaces by the addition of an alloy which melts at a low temperature. The common solders are mixtures of lead and tin (sometimes bismuth, copper, and zinc are added). Jewellers' solders contain copper, silver, and gold.



# LIST OF WORKS ON CHEMISTRY RECOMMENDED FOR FURTHER STUDY

Name.	Author.	Publisher.
<i>Organic Chemistry—</i>		
ORGANIC CHEMISTRY ...	{ Bernthsen (ed. by) Sudborough }	Blackie & Son, Ltd.
CHEMIE DER KOHLEN- STOFFVERBINDUNGEN }	Richter	Fr. Cohen (Bonn)
ORGANIC CHEMISTRY ...	Holleman	Wiley
<i>Inorganic Chemistry—</i>		
TREATISE ON CHEMISTRY...	Roscoe and Schorlemmer	Macmillan & Co., Ltd.
PRINCIPLES OF INORGANIC CHEMISTRY ... }	Ostwald	Macmillan & Co., Ltd.
<i>Physical Chemistry—</i>		
THEORETICAL CHEMISTRY	W. Nernst	Macmillan & Co., Ltd.
INTRODUCTION TO PHYSI- CAL CHEMISTRY ... }	James Walker	Macmillan & Co., Ltd.
ELEMENTS OF PHYSICAL CHEMISTRY ... }	H. C. Jones	Macmillan & Co., Ltd.
<i>Applied Chemistry—</i>		
ELECTROCHEMISTRY ...	Blount	A. Constable & Co., Ltd.
CHEMISTRY OF DYESTUFFS	Georgevics	Scott Greenwood
<i>Various—</i>		
RADIOACTIVITY ... ..	Rutherford	Cambridge University Press
THEORY OF SOLUTION ...	Whetham	Cambridge University Press
PRACTICAL METHODS OF ORGANIC CHEMISTRY }	Gattermann	Macmillan & Co., Ltd.
AUSGEWÄHLTE METHODEN DER ANALYTISCHEN }	Classen	Vieweg (Leipzig).
CHEMIE ... ..		
HISTORY OF CHEMISTRY ...	Meyer	Macmillan & Co., Ltd.





# PHYSICS

BY

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# PHYSICS

## CHAPTER I MEASUREMENTS

Physics at all times has been closely bound up with the science of measurement; until we have measured a quantity we can know but little about it. Thus the huge strides made during the past half-century in our knowledge of the interactions of substances among themselves, and between matter and the ether, have been dependent upon improvements in experimental means of estimating lengths, periods of time, and masses.

### MEASUREMENT OF LENGTH

In the measurement of ordinary lengths, in the weighing of everyday substances, methods of precision have been introduced far exceeding in delicacy anything that was known even twenty years ago, and devices which allow readings to be made more quickly have contributed their effect on the accuracy with which we can measure quantities liable to comparatively rapid variations in time.

**STANDARD ARC OF MERIDIAN.**—The accurate determination of lengths needs a standard yard or metre which shall be free from errors due to the expansion produced by changes of temperature. The alloy of nickel and steel, known as **INVAR**, is practically unaffected even by extremes of heat or cold; thus the determination of the great African arc of meridian is being carried out by the aid of an invar wire, with the International Metre of the Paris Archives as the ultimate standard. When linked up with European surveys the arc will fix a length nearly one-third of the circumference of the globe, from the North Cape to the Cape of Good Hope.

**SMALL LENGTHS—SEARLE'S EXTENSOMETER.**—Small lengths must often be determined also, and here the fine adjustment given by screw motions is of service. In the simple apparatus of **SEARLE'S EXTEN-**

SOMETER, to measure the change of length of a wire under a stretching weight, we have a nearly straight, and therefore very sensitive, spirit level,

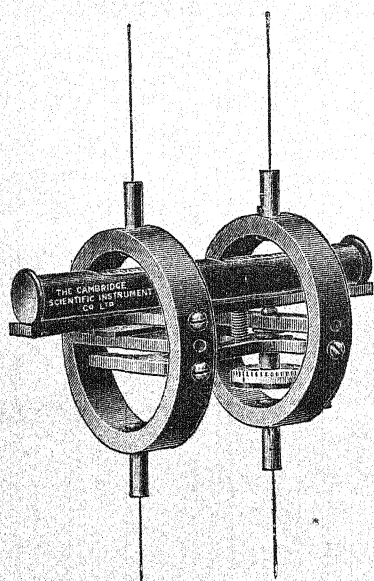


Fig. 73.—Searle Extensometer

one end of which is fastened to a fixed wire (fig. 73). The other can be racked up or down by a screw with a fine thread, attached to the wire which is to be stretched. Increase of length thus causes the level to slope slightly. The pitch of the screw is precisely known, and the circumference of its head is divided into 100 equal parts; the amount of extension of the wire is thus at once read off by the fraction of a turn necessary to bring the level back to the horizontal once more.

EWING'S METHOD.—With somewhat more complicated apparatus, and microscopic observation, Ewing has devised a means of measuring the stretching of a rod or wire to the millionth part of an inch, say the three-thousandth part of the thickness of a page of this book.

### MEASUREMENT OF MASS

CURIE BALANCE.—In weighing, the CURIE BALANCE may be cited as an instrument in which precision is united with quickness (fig. 74). Instead of the nice adjustment of weights necessary in ordinary methods, only approximate balance is obtained, and the deflection of the pointer read off by a suitable microscope. This gives instant measure of the further accuracy required. The air cushion formed by the play of pistons in cylinders below the scale pans "damps" the swings of the beam, and so brings the pointer almost immediately to rest.

### MEASUREMENT OF TIME

USE OF INVAR AND QUARTZ.—In time measurement perhaps less striking advance has been made, though the accuracy of modern time keepers is very great. Here again invar has come to our aid in the construction of pendulums and springs which are independent of temperature so far as expansion is concerned. Threlfall, too, makes the



interesting suggestion that quartz hair springs are fairly easily constructed, and are likewise free from changes in length and stiffness when heated or cooled.

TIME.—For time, however, we cannot make a material standard, as we can for length and mass, and our units depend on the length of the day, which we know to be subject to small periodic changes and to a gradual lengthening as the earth slows down in its rotation. Thus our standards are slowly changing, and we can of course never measure the

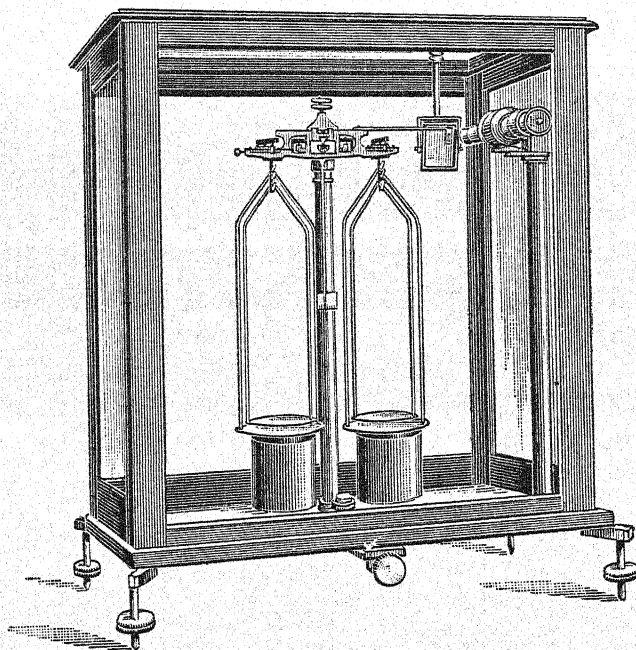


Fig. 74.—Curie Balance

change by ordinary clock methods, which rely ultimately on the length of the day itself; we might as well endeavour to measure the expansion produced in a brass rod when heated by engraving a scale upon the brass itself. But we now know that many physical changes take a definite time in which to occur, and this time is quite independent of astronomical changes. Thus the discharge of an electrical condenser under fixed conditions occupies a measurable period, so this may be used as an ABSOLUTE STANDARD OF TIME, and if, on comparing experiments made now and a hundred years hence, we should find that the number of discharges per second has altered we shall have measured the change not of the actual time of discharge but of the second, the time unit in which it is measured.

## OTHER ASPECTS OF MEASUREMENT

QUARTZ FIBRES OF C. V. BOYS.—In sensitiveness of adjustment improved materials of construction have everywhere led to progress, and in no instance perhaps has this advance been more striking than in the extraordinary delicacy with which light deflectable parts of instruments (*e.g.* the radio-micrometer, p. 184) can be suspended by means of the fine QUARTZ FIBRES first produced by Mr. C. Vernon Boys. These fibres, briefly, are made by fusing quartz in the flame of an oxy-hydrogen blowpipe, and affixing a small quantity to the shaft of a little arrow, which is then fired from a diminutive crossbow. In its flight the quartz is drawn out into fibres, some as small as  $\frac{1}{300000}$  in. thick, a thinness compared to which a fibre of unspun silk is as a cable to a cotton thread. These quartz fibres yet possess a strength enormous in comparison with their diameter, and also offer a constant and reliable resistance to twisting, the property which renders them so useful as suspensions for light bodies.

USE OF LIGHT AND ELECTRICITY IN MEASUREMENT.—Light waves, electrical resistance, the electrical effects of heat, electrical induction, and many other physical phenomena have been pressed into the service of the art of measurement, so that it is no hyperbole to say that we measure space and time by coloured lights, and weigh bodies and record their temperatures by electricity.

MEASUREMENT IN OTHER SCIENCES.—Not in physics alone have these methods been employed; in chemistry, in physiology and the medical sciences, in zoology and botany exact measurement is becoming more and more important. Physical chemistry is almost another name for molecular physics; modern works upon physiology at a casual glance might almost appear to be electrical treatises; while in biology Professor Pearson and his fellow workers have founded a mathematical school based entirely and necessarily upon measurement.

## NOTATION

Physics, often dealing numerically with vastly great and with minutely small quantities, has been led to adopt a shorthand system to avoid the long strings of noughts which would otherwise encumber calculations. This system is to denote numbers by a few UNITS multiplied by the necessary powers of ten. Thus, for instance, 34 is  $3.4 \times 10$ , 340 is  $3.4 \times 100$  or  $3.4 \times 10^2$ . Such notation is, of course, more awkward than writing the number in the usual way; but if we wish to express 34 millions,



34,000,000, we at once see the advantage of contraction to  $34 \times 10^6$  or  $3.4 \times 10^7$ . Again, in small quantities .34 may be preferable to  $3.4 \times 10^{-1}$ , and even .034 to  $3.4 \times 10^{-2}$ ; but .0000034 is certainly clumsier than  $3.4 \times 10^{-6}$  as the expression for 3.4 millionths.

This system is used to some extent in later pages; for example,  $3.4 \times 10^{-10}$  will be used to express 3.4 ten thousand millionths, or the decimal point followed by nine ciphers before the figures 34; again,  $4.5 \times 10^{26}$  will mean 450 billion billions, 45 followed by 25 noughts.

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## CHAPTER II

### MOTION

Physics has been described as the science of motion, and certain it is, in any case, that no study of the subject can progress any distance without an exact knowledge of the varied forms of motion and of the "laws" which describe them.

**NEWTON'S LAWS.**—The simplest imaginable case, though one perhaps never occurring in nature, is that of uniform speed in a straight line. Newton, in his far-reaching laws, first showed that this is the natural motion of a body free from all external influences. As soon as the body has an environment—other bodies or electric charges or sometimes magnets—its motion changes in speed or direction or both. Such changes are always associated with the environment, and the more nearly we can isolate a body from such external influence the more nearly does its motion become the simple kind mentioned.

The law is entirely an experimental result, but it carries something of the air of a self-evident truth, probably because everyday life affords constant rough-and-ready illustrations of its working. These illustrations lie all around us in the need for some action to start the motion of a stationary body, to stop it when it is moving, even to change its speed or to divert it from its course. When it stops "naturally", there is friction to account for the change; if it falls, there is its own weight, that is the pull of the earth, which has drawn it downward.

**FORCES.**—Friction and the pull of a weight can be detected by the senses, the so-called muscular sense, and such experiences have led to the notion of FORCES acting upon bodies, and determining their change of motion, so that Newton's laws go on to say that a body only changes

from uniform straight-lined motion under the action of a force. Different forces, then, are to be compared by the change of speed, or, better, by the rate of change of speed which they produce; the greater the force the more rapidly does it get up speed in a body, and the direction of motion is the direction of the force.

INERTIA.—But when we apply forces to different bodies we meet with a difficulty. The same action does not always produce the same speed, and these variations can only be due to some property of the bodies themselves. It is a sort of reluctance to move, for the bulkier a lump of a given substance the more slowly does it respond to a given force. To this passive resistance the name of INERTIA is given, and its measure is the MASS of the body.

WEIGHT AND MASS.—The WEIGHT of a body is often confounded with its mass, but an example will both clear up the distinction and show the dependence of the more familiar weight upon the other quantity. A 1-lb. "weight" is a body which is attracted by the earth with a force which we are accustomed to call "one pound". If we could take it to the moon it would weigh much less, because our smaller satellite could not attract it so strongly as does the earth. The difference is between the earth and the moon, and is not a change in the "pound weight". If we use the body as the projectile of a gun, then the velocity with which it leaves the muzzle is the same whether we fire here or in the moon. The reluctance to move is unchanged and depends only on the size and substance of the body. This is what we mean when we say that the mass of a body cannot be changed however we treat it. In chemical changes and in melting and boiling we may transform it into other forms of matter, but if we could collect it all and apply equal actions to it before and after the changes we should find that it gained speed equally in the two experiments, so that its total inertia had remained unaffected through all vicissitudes.

This is the CONSERVATION OF MASS, upon which chemistry as a quantitative science depends; for ordinary purposes, certainly to one part in a million, mass does remain constant. Of its *absolute* constancy there is some doubt, and experiments by Landolt and Heydweiller seem to show that copper sulphate dissolved in water forms a solution which is very slightly lighter than the sum of the separate salt and water. In other words (since the earth's pulling power cannot have been affected) the mass is reduced in the process of solution. Other instances of what appear to be true changes of mass will be discussed when we come to the fast-moving particles shot out by radium.

ENERGY.—Motion, then, needs some definite action to produce, change,



or destroy it, because of the inertia of matter, and the ability of an agent to cause such change appears to be lessened or altogether lost in the process. Thus a spring in uncoiling will drive a clock, gunpowder in exploding propels a bullet, water in falling turns a wheel, but once this uncoiling, explosion, or fall is ended, the ability to cause the appropriate action ceases. The processes quoted and others which will occur to the reader are instances of the "doing of work", as we say, so that in a system capable of causing motion there appears to reside a power to do work; this power is termed ENERGY.

POTENTIAL AND KINETIC ENERGY.—The coiled spring and the gunpowder have energy in virtue of the position of their parts or their molecules, the water in virtue of its position above the wheel. Such energy is called POTENTIAL, and makes itself apparent in the motion of the spring or bullet or falling stream. The water in its fall turns the wheel, and so still possesses energy, now due to its motion, KINETIC energy. This is only gained in falling as a result of its previous potential energy. So again with the bullet, work is done when it strikes a target, and this work comes from the kinetic energy of the flight. Careful measurements show that energy may be passed on in this way from one substance to others, from one form to others, but its total quantity is never increased or lessened. An obvious first objection is: What then of the energy lost when a bullet is embedded in a sandbank or flattened against a target? The answer is that work is spent in heating the bullet and the sand or target, and that the heat itself is one form of energy. The full reason for this we must leave for the present, but one has only to think of the heat produced by the brakes of a railway train, and the work produced by the heat of its boilers, to see that, in some sense, heat and work are convertible terms.

CONVERSION OF ENERGY.—Energy is thus convertible through a long chain of processes; we may suppose, for instance, that the energy of the heat from the sun evaporates water, forming clouds, and from them in rain is produced a mountain stream; this in its course turns water wheels which drive electrical machinery; by a quite possible imaginary process, the electric currents might be used in a distant factory to build up chemically some unstable and explosive compound, in its turn driving the bullets in some far-off battle, or perhaps employed in a drought to fire upon clouds and induce such a rain shower as started the cycle of changes.

CREATION OF ENERGY IMPOSSIBLE.—The last idea may possibly suggest that we can create energy, for the shower brought on by a small quantity of explosive may conceivably do work enough for the manufacture of a much larger quantity. But it must be remembered that the shot

has not raised the water in the cloud; the energy for that has already been supplied by the sun. We may, in a sense, steal energy from nature in this way, but we can never increase the total amount in the universe by so much as would disturb the lightest feather.

**ACCELERATION.**—When a moving body changes its speed it is said to be **ACCELERATED**, the acceleration being measured by the speed added (or taken away) in each second. Sometimes the speed increases steadily, as in the case of a falling body; the acceleration is then, of course, constant, and the space passed over per second increases more and more rapidly as time goes on.

**MOVEMENT IN A CIRCLE.**—There may, strange though it appears at a first glance, be acceleration without change of speed. Thus a body moving round and round a circle at uniform speed has the direction of its path constantly altered, and a definite speed must be added to it in each second of its motion to keep it in its circular track; otherwise it would fly off at a tangent to the circle. The amount added per second is the acceleration, and its direction is always towards the centre of the circle. For if it were not thus at right angles to the direction of motion it would have some quickening or slowing influence upon the actual speed, which is to remain constant. Thus the body, by reason of its inertia, always tends to fly off in a straight line, is constantly being brought back towards the centre of the circle, and consequently is using up energy. In other words, such a revolving particle must constantly dispose of a certain amount of energy, which may be manifested in any of its forms. One important instance of this lies in the fact that a revolving electrified particle in the same way emits a quantity of energy, and this takes the form of waves sent out through space at enormous speeds. One result of such waves is the electric disturbances utilized in wireless telegraphy; in another aspect these waves make themselves known as light.

**MONORAIL.**—A great deal of attention has recently been directed to a monorail vehicle which keeps its equilibrium, even when at a standstill, with no extra support. This is brought about by the so-called **GYROSTATIC ACTION** of a large spinning top supported on the vehicle and revolving about a vertical axis. The power required to drive this top is only a small percentage of that needed to propel the carriage; so there may be large economy in the use of such vehicles, in the saved cost of laying and materials of a second rail, and in the friction of extra wheels.

This gyrostatic action is simply that by which a child's spinning top maintains its upright position and resists being upset. Press a finger against a well-spun pegtop; it squirms along the finger and strives to



regain its old vertical position. Even a smart blow, unless very violent, merely pushes it bodily along to continue spinning in a new spot without tumbling over.

**BALANCED GYROSTAT.**—Still stronger instances of this tendency of a rotating body to keep the direction of its axle unchanged is shown by a balanced gyrostat, such as is shown in fig. 75. It is a heavy top, so supported and supplied with a counterpoising weight that it will rest with its stem pointing in any direction; when it is not spinning a light touch will swing it about its pivot. But set it spinning in the ordinary way by wrapping a string around the axle and pulling it smartly off again; then in whatever direction the top points, in that direction it persists, and quite violent pressure is required to push it aside. Such a gyrostat of large size, with a vertical axle and spun by machinery, is the steadying mechanism of the Brennan car.

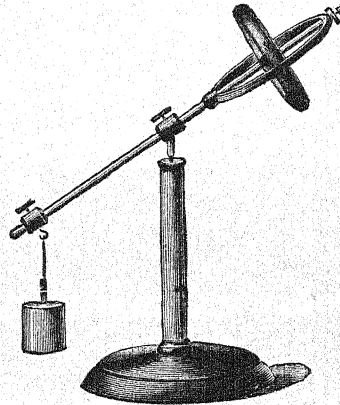


Fig. 75.—Balanced Gyrostat

**SIMPLE HARMONIC MOTION.**—Still another case of motion (fig. 76), one of the most important, is that in which a body starts from a point A with a certain acceleration, which then grows less and less until it vanishes at O. Up to this point the body has moved continually faster, being accelerated towards O, and if the acceleration vanished permanently it would now travel on indefinitely with the final speed attained. But the acceleration only ceases for an instant and then reappears in the reverse direction, steadily increasing as before it diminished. In other words, the body moves on, but more and more slowly, until at last it comes to rest at B, as far

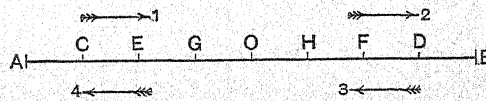


Fig. 76.—Simple Harmonic Motion

from O as when it started at A. The acceleration then pulls it back, as marked by arrow 3, diminishing as before, reversing at O. The body thus returns to A, whence it commences a second similar journey to B and back, and so on indefinitely. If the acceleration is reduced from its full value by amounts proportional to the distance from A or B, so that at C or D it is three-quarters of its maximum value, at E or F a half, at G or H a quarter, then the motion is called SIMPLE HARMONIC MOTION, and is much the same as that of the piston of an engine in its stroke,

or of the bob of a pendulum, though here the vibration is along a small arc of a circle.

**DOUBLE-PENDULUM MOVEMENTS.**—Peculiarly beautiful and complicated motions result from the compound motions of two pendulum-like swings at right angles to each other. Take, for instance, the knob of a long hatpin stuck firmly into a wooden base and set vibrating. Its motion may be like that of a pendulum bob, in one line only, but more commonly a tap will set it quivering in a more or less curved path, a circle, or an oval. This motion can be made up of two sets of swings at right angles. A tap from left to right sets the knob vibrating to and fro,

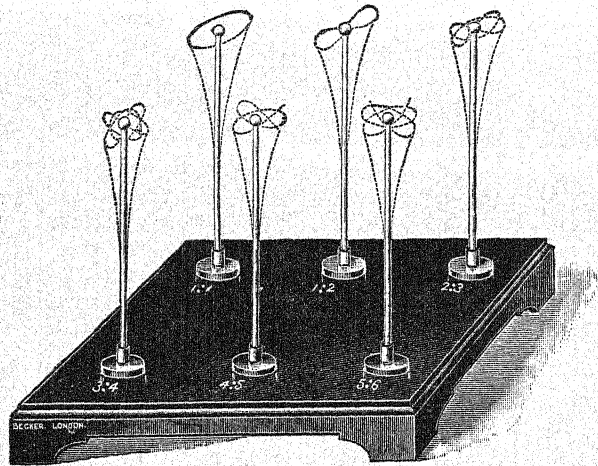


Fig. 77.—Wheatstone Kaleidophone

and a second tap, perpendicular to the first, at once brings out the curved path, which is readily seen as a whole, due to the persistence on the retina of the image of the quickly moving head.

**WHEATSTONE KALEIDOPHONE.**—Wheatstone's kaleidophone is such a series of vibrators, except that the "pins" are made oval instead of cylindrical, so that the two sets of vibrations are more distinct, and are executed in different periods. Fig. 77 shows the curves thus obtained.

**CURVED-PATH VIBRATIONS.**—A pendulum bob can be caused to swing in various circular and oval curves, and the remarkable patterns in the accompanying plate were produced by the compounding of two such curved-path vibrations. An inking pen is attached to the lower end of a long heavy pendulum capable of swinging slowly in various curves. The paper upon which the trace is obtained is fixed to a little table on top of a second pendulum supported at a point some distance below the paper. Thus similarly varied curved motions can be imported to the table, and



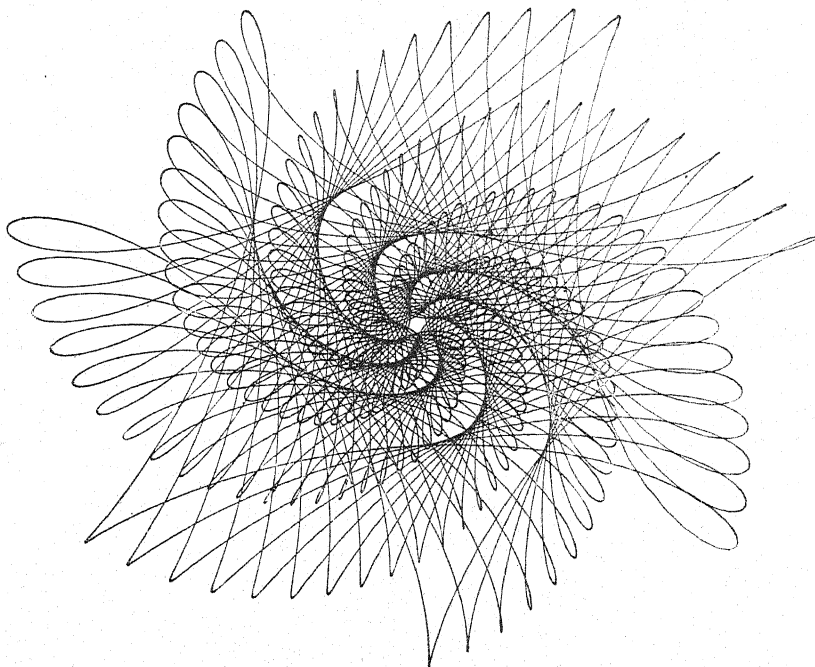
### HARMONIC CURVES

These curves illustrate the complicated motion of a pendulum swinging in an oval path, and carrying a pencil, relatively to a second pendulum swinging similarly and carrying a card upon which the pencil traces the patterns shown. Slight alteration of the path of either pendulum causes great changes in the figures.

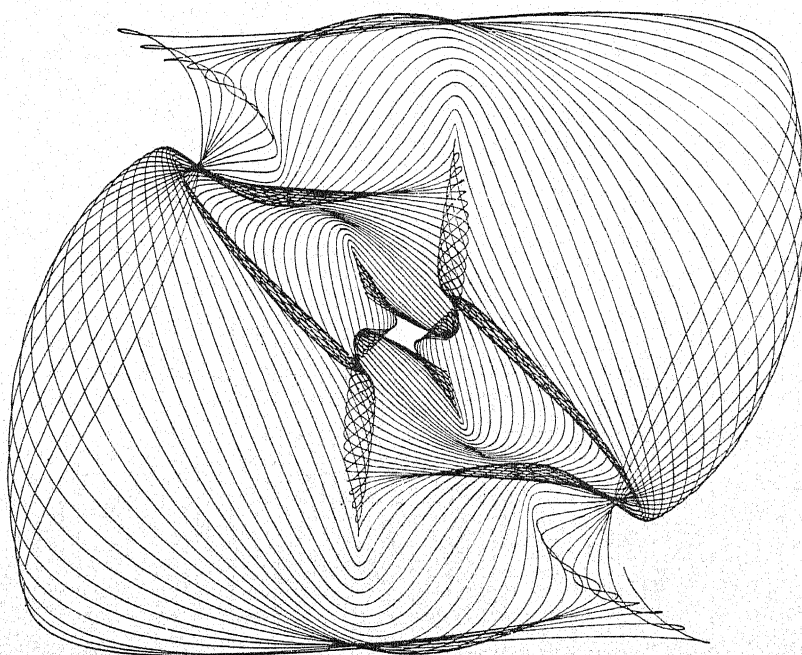




A



B



HARMONIC CURVES





the combination of the two produces figures of such extraordinary complexity and variety as the specimens shown. Friction and air resistance cause the swings to become continually smaller, so, that the pen never exactly repeats its path on the paper, but tends always on the whole to approach the middle point, where ultimately it would come to rest. The individual forms of the various patterns obtained depend upon the particular starting pushes given to the two pendulums, and to the rate at which the swings in various directions occur and die away.

LONGITUDINAL WAVE MOTION.—Suppose we have a whole host of particles in a line, and the one at the end is made to vibrate to and fro in the line of the particles. In moving forward it presses upon the next, and so, a brief instant later, this moves forward too, affecting the third, and that the fourth, so that an impulse runs along the whole line. If the balls are not connected together in any way, that is an end of the matter, even if the first particle is still kept in vibration; but if the particles are connected by short, light spiral springs, then the first ball compresses its spring and passes on the impulse without actually touching the second, and then on its return tends to drag back the second after it. This springy push-and-pull action is transmitted along the whole row, so that finally each ball is describing simple harmonic action. But the line is not swinging to and fro as a whole; the first ball has moved an appreciable distance toward its neighbour before the latter starts on its course, and the third is a little later still. Thus there is a disturbance which travels at a definite speed along the row, though the balls themselves maintain the same average position. The motion of the balls needs work to be done against the elastic forces of the springs, so that energy is steadily passed along the system. Such a state of things is known as a WAVE MOTION; the essential feature is that there is a passage of disturbance and of energy, but no carriage of matter as a whole in the direction of the waves.

The particular case we have described is a longitudinal wave motion, longitudinal because each ball moves to and fro in the direction of progress of the waves. These latter are waves of alternate compression and rarefaction, each ball approaching and then receding from its next neighbour, which itself goes through similar evolutions an instant later.

TRANSVERSE WAVE MOTION.—If the springs resist bending, a wave motion can also be propagated along the line of balls by shaking the first ball regularly to and fro at right angles to the line. The wave in this case is transverse, and takes the characteristic "wave" form which has given its name to all this class of motions.

WAVES OF THE SEA.—The sea affords an excellent example of trans-

verse waves. In deep water far from the shore the disturbed particles of water simply move up and down along such straight paths as the diagram shows (fig. 78). But each has reached a position in its course very slightly different from those of its neighbours; it is in a different PHASE of its journey. So if we could take photographs of the topmost particles, we should find the vertical straight lines as the blur representing their track in a time exposure; but a snap shot would reveal them in such positions as those marked by dots.

Such waves as these are set going by the weight of the water if one part is by any means brought to a higher level than the rest. Its weight pulls it down, and, getting up speed in the fall, its inertia carries it below the true water-level; so instead of a hump, there is a hollow of the surface. It again seeks its proper level and rises, only to overshoot the mark once more, and so on till the friction of the water particles brings it to a stand-

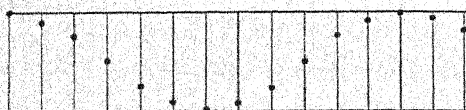


Fig. 78.—Wave Motion

still. Meanwhile this disturbed part has set the water round about it into a similar state of vibration; and this, started perhaps in the first place by the dropping of a stone in a pond,

or the lash of the wind on the sea, spreads away as a system of waves in all directions.

**WAVE LENGTH.**—The length of a wave is measured from one crest to the next, or one trough to the next; or in the longitudinal waves it is the distance between two successive compressions or two successive rarefactions. In either case it is the distance travelled by the wave in the time that any one moving particle takes to complete a to-and-fro vibration. This time is called the PERIOD of the vibration; the number per second is the FREQUENCY. Waves may travel along what is practically a line, such as a stretched string, over a surface, as with water waves, or through a volume, as in such cases as sound and light. The line or surface marking the forward limit of a wave at any instant, the boundary across which it is about to pass, is called a WAVE FRONT. In waves travelling straight forward it is thus a straight line or a plane, while in the case of waves spreading out from a centre the fronts are circles or spheres drawn about that centre.

In the case of water waves the speed of the waves depends on their length, long waves travelling faster than shorter ones, down to the length of about  $\frac{2}{3}$  in. For still shorter waves the speed increases again, so that, for instance, waves 1 yd. long move at the same speed, viz. about 3 miles per



hour, as those whose length is only  $\frac{1}{10}$  in. The minimum speed is nearly  $\frac{1}{2}$  mile per hour.

**INFLUENCE OF CAPILLARITY.**—The reason of this peculiarity is that besides the weight of the water there is a surface force of capillarity (p. 169) tending to drag protruding parts back to the level again. This force only becomes important when the waves are quite short, so that the curvature of the surface is comparatively great. On the other hand, the gravitational effect is greatest with a long wave. Hence, whether we start with very long or with very short waves, we find greater speeds than with those of intermediate lengths, when neither influence has its full effect. The shorter waves, say of  $\frac{1}{10}$  in. and less, which are mainly under the control of the capillary forces, are usually termed ripples.

**WAVES OF SOUND AND LIGHT.**—Transverse waves may be sent along a string—stretched by a weight or by screwing up a wrest pin—either by plucking the string with the finger, by tapping it with a small mallet, or by bowing it as a violin string is bowed. Here the stretching tension tries to keep the string straight, and supplies the force which vibrates the cord back and forth. This force does not depend

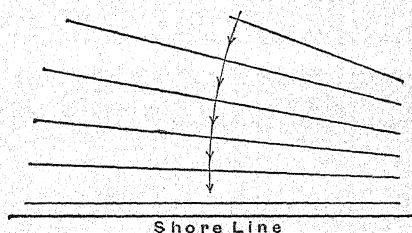


Fig. 79.—Refraction of Sea Waves

on the length of the waves, so the velocity is also independent of the wave length. This is a general feature of those waves in which the vibrations are maintained by elastic forces, as in the cases of sound and light waves.

**REFLECTION OF WAVES.**—Waves in general have certain characteristic properties. They can be reflected when they fall on an obstacle in which they travel less rapidly or not at all,<sup>1</sup> *i.e.* upon objects more or less impervious or opaque to them. A water wave impinging on a retaining wall is clearly reflected, and the return waves travel away from the wall at the same speed as those which are falling upon it.

**REFRACTION OF WAVES.**—Waves, too, suffer refraction, *i.e.* they are bent round and change their direction on entering a new medium in which they move with different speed. Thus a sea wave is bent as it approaches the coast (fig. 79). Suppose it is running in obliquely, then the nearer end, passing over the shallower places, moves slowest. The farther end gains on it, and the whole wave front swings round as long as there

<sup>1</sup> Reflection also occurs at the surface of a medium in which they can travel more rapidly, *e.g.* when light passes from glass into air some is reflected; hence the doubling of the reflected images in a thick piece of plate glass.

is any difference in the distances from the shore of the two ends. Thus the wave finally comes in parallel to the shore line at whatever angle it originally approached. This is a sort of continuous refraction, but when a wave passes suddenly into shallow water over a flat submerged mass of masonry the bending is quite abrupt.

**WAVE SHADOWS.**—Waves can turn corners to some extent. If the waves are long, and the obstacle to their progress but small, the "shadow" it casts is very slight; but a large object distinctly screens the space beyond from disturbance by the waves. A harbour is thus "shaded" by its walls from the sea waves, which only ruffle the surface when moving straight through the entrance.

**INTERFERENCE.**—Two substances can never destroy each other, but two equal and opposite motions can obviously do so; and, more generally, each motion imparted to a body alters the way in which it travels. Thus, if two similar systems of waves are passing through the same space, the motions of the vibrating bodies or material making up the waves are determined by the influence of both systems. In such a case we are said to have **INTERFERENCE**. If the two sets of waves are travelling in the same direction, crest to crest, they merely increase each other's effect; but if they are moving crest to trough they everywhere neutralize each other, and the result is a waveless calm. This is not a practical case, however; what usually happens is that the waves reinforce one another in some places, while in others their effect is a more or less complete calm.

The interference of water waves is sometimes quite beautifully shown when short waves impinge obliquely on a sea wall. They are reflected, and the direct and reflected waves are in the best condition to interfere, forming a dappled surface which reflects the sunlight in ever-moving patterns.

**STATIONARY WAVES.**—An important case of the reflection and interference of waves is that when the waves run in perpendicularly upon the obstacle. Stationary waves are formed, *i.e.* waves in which certain parts are always at the dead level while the regions halfway between them are alternately crests and troughs. An analogy may explain what occurs. Suppose we paint two long glass strips with the same coloured transparent paint, not evenly, but so that as we glance along either strip we find a graduation of tint, from clear glass up to the thickest paint and as gradual a diminution again, this being repeated several times in the length of the strips. The darkest places may stand for wave troughs, the clearest for crests, while the parts of the wave which are neither raised nor depressed are represented by the medium colour. Lay these together, so



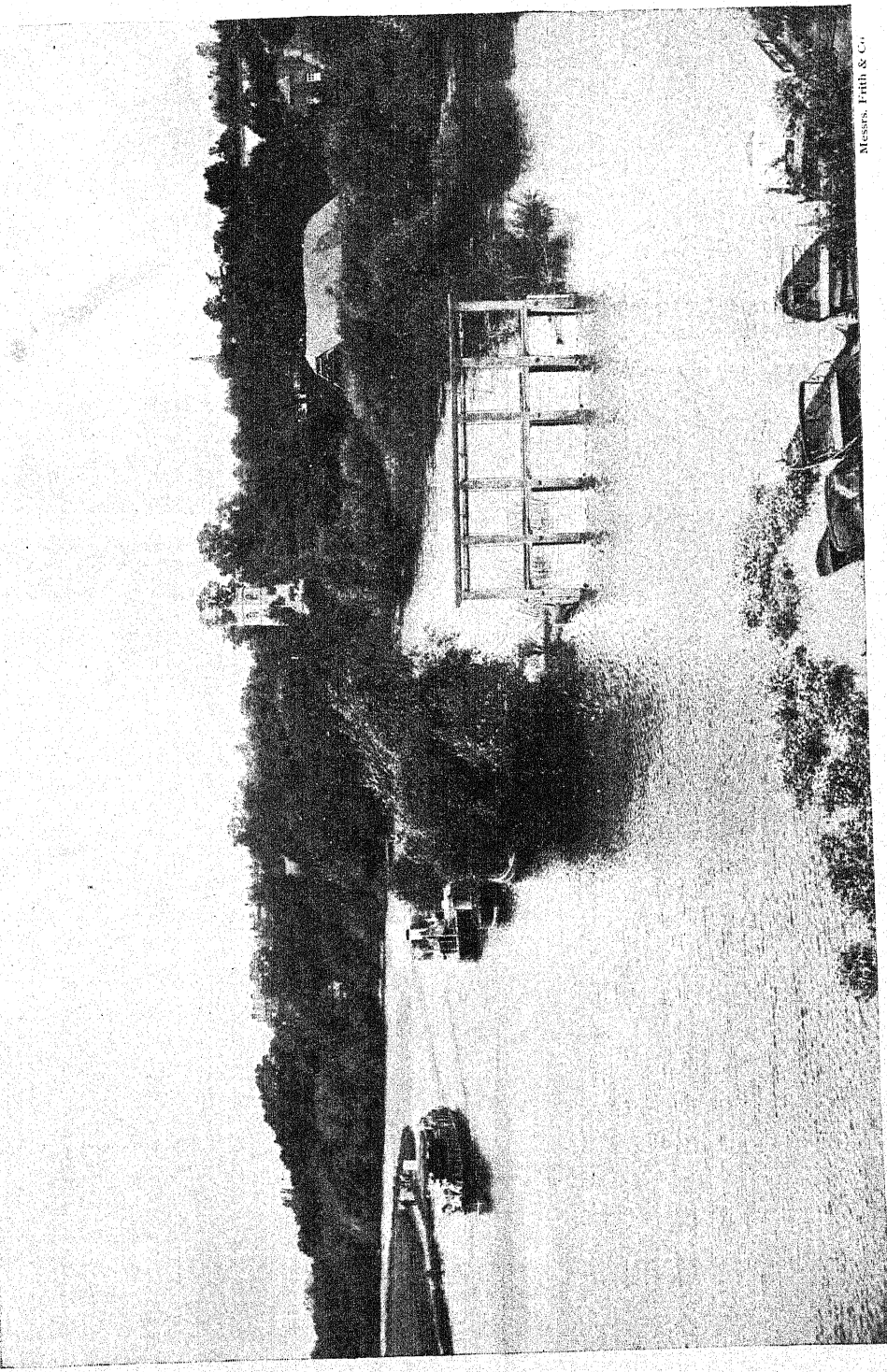
### INTERFERENCE OF WATER-WAVES

The two sets of waves which pass around the island show interference patterns in the foreground (especially well marked in front of the dark reflection of the island).

Observe also the bow wave set up by the moving steamer, which is moving faster than the waves themselves.







Messrs. Frith & Co.

INTERFERENCE OF WATER-WAVES





that crest coincides with crest; then the appearance is the same as for one slip with greater contrasts. Next slide the two past each other in opposite directions at equal speeds, and keep the attention fixed on a dot on the table beneath. If the dot was at first under a crest, the glass above it will gradually grow darker till the "trough" effect is reached, and the changes begin again in the reverse order. The same variations occur if a trough is selected as the starting-point; but if an average coloured spot is selected the colour will appear nearly uniform as the plates move across, because a growing depth of colour in one plate is just neutralized by an approach to the clear glass of the other. So when two trains of equal waves meet squarely the effect is similar; some parts oscillate between crests and troughs, neighbours being always in the opposite conditions. Between these violently disturbed regions lie others which are always calm. These quiet points are called **NODES**.

**SAND RIPPLES.**—Mrs. Ayrton has shown that the sand ripples of the seashore owe their existence to the disturbances of such stationary waves, which pile up the sand at points halfway between the nodes. Their appearance is so local and in such isolated patches because they are always wiped out by the edge of the waves when the tide falls, except when they lie in a depression deep enough to keep them covered by a pool until the tide has left them. Mrs. Ayrton recently made a suggestion which may be of the utmost importance. The dreaded Goodwin Sands, she finds, have every appearance of being great sand ripples deposited by the action of stationary waves set up by the particular run of the local currents, and it is asked if it is not possible so to divert some of these currents that the dangerous sand piling may cease and the present sands be gradually swept away by the altered flow of the tides.

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### CHAPTER III

## PROPERTIES OF MATTER

**THREE STATES OF MATTER.**—Turning from general ideas of motion to the distinctive properties of matter, we are at once met by the possibility of the existence of substances in three different states. Solids, on the whole, offer some amount of elastic resistance to a change of their shape or size; liquids suffer change of shape under the smallest conceivable forces, even those of their own weight, while yet resisting change of

bulk almost as strongly as a solid. Gases, though resembling liquids in their readiness to undergo shape changes, have no definite volume at all, but alter their bulk with the pressure acting on them, always filling the vessel in which they are placed.

COMPRESSION.—All substances yield to some extent to uniform compression; thus an added pressure of 1 ton to the square inch would diminish the volume of air 150 times, but with water would only produce a compression of 7 parts in 1000, and with iron only 1 part in 10,000. Even in the last two cases, however, it is clear that there must have been some space for the water or iron to be compressed into, that the liquid or solid cannot really have the absolutely continuous structure which it appears to have. Still more in the case of air it is evident that the "air-stuff" fills only a tiny fraction of the apparent "air-space". There is, then, no escape from the conclusion that matter is discontinuous, "coarse-grained"; if we could be endowed with indefinitely sharp sight we should see, not a regular greyish solid or colourless liquid, but hosts of tiny particles, separate and distinct one from another. Air also would present the same appearance, except that the particles would be far apart, as scattered in proportion to their sizes as the stars in the heavens.

DIFFUSION.—The expansion of bodies when heated points in the same direction, but perhaps more direct evidence arises in the phenomena of diffusion. If a heavy gas like chlorine is poured into a tall jar, displacing the air, until the jar is half full, we can distinguish its upper surface by the colour of the gas. After a time the colour is found to have spread up the jar, showing that the heavy chlorine has diffused up and the lighter air down until the mixture is complete. It is for this reason that air can exist as a mixture of oxygen and nitrogen, with no greater proportion of the heavier oxygen at the sea-level than on a mountain top.

Liquids, too, diffuse into one another. Half-fill a glass with clear water, immerse the stem of a funnel down to the bottom, and pour steadily into it a strong solution of copper sulphate. This heavy, dark-blue liquid settles under the water with very little mixing, so that there is an abruptly marked boundary. Let the glass stand undisturbed for a few days, however and the blue solution diffuses up through the water in spite of gravity, so that the colour shades evenly from light to dark, and finally becomes the same all through the liquid.

DIFFUSION OF SOLIDS.—Even solids diffuse into one another. The late Sir William Roberts-Austen, while Master of the Mint, placed pieces of lead and of gold in firm contact, at the ordinary temperature of the



air. Four years later he found gold in appreciable quantity  $\frac{1}{8}$  in. deep in the lead, while nearer the surface,  $\frac{1}{30}$  in. deep, it had diffused in to the amount of over 1 oz. per ton; an ore of equal richness could be worked with profit.

Here we have clear enough evidence of the existence of separate particles making up matter, the molecules of the chemist. And further, these molecules must be in a natural state of motion, otherwise these facts of diffusion become unintelligible.

**GASES.**—Gases are in many respects the simplest of bodies, and it is not surprising that we must turn to them for the next extension of our views. Let us try whither we are led by the bold hypothesis that a gas is made up of tiny separate molecules in motion. To commence with, the motion must be indiscriminate; that is to say, no more molecules can be moving in one direction than in any other, or we should have a flow of the gas as a whole. The molecules, too, must be small and many. They move in straight lines until their motion is affected by the nearness of other molecules or the sides of the vessel containing them. They strike against the others and against the sides, upon which, by their oft-repeated blows, they produce the effect of a steady pressure. If a movable piston forms part of the vessel it is forced outwards, if we screen its outer side from the impacts by removing the air from that side by a pump. All this is in accord with the well-known expansive tendencies of a gas, and its ability to fill any vessel, however great. The pressure is to be measured by multiplying the number of blows per second on a square inch of surface by the impulse of each blow, and this depends on the speed of the molecules. Calculations of this last can be made from the known pressure and density of the gas. The average speed proves to be great, and varies with the gas used. It is inversely proportional to the square root of the density, so that, for example, hydrogen molecules are hurtling to and fro at four times the speed of the sixteen-times-heavier oxygen, viz. 4000 miles per hour, on the average, to oxygen's 1000.

**SPACING OF GAS MOLECULES.**—The average distance apart of gas molecules is so great as compared with their sizes that they are practically free from each other's influence, so far as the ordinary gravitational attraction is concerned. Their only interactions are the changes of velocity brought about by their collisions. What, then, will happen if we halve the volume of the gas by thrusting a piston slowly in. Evidently we pack the molecules closer together, and their collisions with each other and with the vessel become more frequent. Each molecule moves at the same speed as before, but there are twice as many in each inch cube of space,

so twice as many strike each square-inch face per second after the compression. The forces of impact are thus doubled, and so we arrive at the simple result that halving the volume doubles the pressure. This is exactly what Boyle long ago found to be true for all gases, and our deduction of it has immensely strengthened our theory, the Kinetic Theory of Gases, as it is called. Numerous other physical laws follow from this theory, of which we have given a bare outline, without detail or light and shade. In the subject of Heat we shall recur briefly to another aspect of the matter.

**LIQUIDS.**—Liquids must have their molecules more tightly packed than gases, but their fluidity suggests that the attractive hold of particle upon particle is still far from complete. It is sufficient to prevent the quick flight of the gas molecule, but not to prohibit slower erratic motion through the liquid mass. Thus the molecule of water has a mass of about  $2 \times 10^{-23}$  grm., and a diameter of perhaps  $10^{-8}$  cm. A cubic centimetre of water weighs 1 grm.; so it must contain  $5 \times 10^{22}$  molecules. It could contain  $2.5 \times 10^{23}$  molecules, five times as many, of the same size, if these were tightly packed in; so in water there is plenty of room for free motion.

**SOLIDS.**—In solids the packing is closer still. Each atom has a space not much bigger each way than the diameter of the atom of the substance, so that the motion must be extremely slight. This explains the greater rigidity or resistance to change of shape. When a solid is bent to and fro the friction between its molecules produces a good deal of heat, as anyone who breaks a rod of solder in this way is compelled to notice.

**TENSILE STRENGTH OF SOLIDS.**—At the short distances apart of the molecules of solids and liquids their gravitational attractions for each other are so great that they may often exceed the weight of the substance as a whole. The great tensile strength of most solids, *i.e.* their resistance to fracture under a direct pull, gives everyday proof of the existence of these forces. 30 tons per square inch are needed to pull a steel bar asunder, while special steels may have tensile strengths of 50 tons or so per square inch.

**SURFACE TENSION OF LIQUIDS.**—In liquids these forces are not so readily observable, because the least pull results immediately in a change of shape, the molecules being, as we have seen, free to move about among each other. The attractions in liquids, however, reveal themselves in other ways, as striking if not so direct. Near the surface of a liquid a molecule will be subject to greater forces pulling it towards the interior than in the reverse direction, because fewer molecules lie on the side of it nearest the surface. The surface layers of molecules are therefore "thinned out", as it were,



by the attractions of the bulk of the liquids, so the surface skin of a liquid behaves as though it were in a state of tension, called the **SURFACE TENSION**.

**CAPILLARITY.**—It is this surface peculiarity which produces the differences in level in liquids in narrow tubes. A certain amount of curvature is always produced at the edges of a liquid surface, because there the liquid is all to one side and the pulls of its molecules are also complicated by those of the solid. Hence, for instance, a water surface bends up at the edges where it touches the sides of the vessel, while mercury curves down, presenting a convex surface. In water, then, the surface tension tends to drag the liquid above its normal level, and the rise is shown in narrow tubes, inside which the whole surface is concave. In mercury the liquid in such a tube is depressed below the level outside. The amount of rise depends entirely upon the curvature of the surface, *i.e.* upon the fineness of bore of the capillary tube (*L. capillus*, a hair), as may be shown by the possibility of supporting quite a large weight of water above its normal level, as in fig. 80, by drawing out the tube of the funnel in a blow-pipe flame to a very narrow diameter.

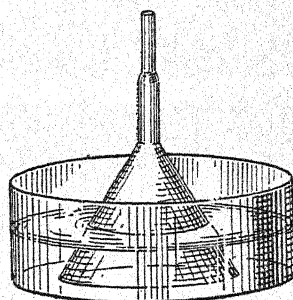


Fig. 80.—Capillarity

Mercury can be kept without leaking in a muslin bag, because the capillary forces acting in the fine meshes of the material are able to overcome even the great weight of the mercury.

A piece of glass with a flat surface pressed down under mercury against the flat bottom of a glass tank remains there, although far lighter than mercury; the capillary force holding it down so far exceeds the upward push of its buoyancy that the whole vessel may be lifted by the piece of glass.

The greater pressure indicated by the tendency of convex surfaces to stand lower than flat ones (as with mercury in a capillary tube) causes such convex liquid areas to evaporate in an atmosphere that is saturated for the same liquid with a flat surface. Thus in air, saturated so far as the water in a pond is concerned, drops of rain may shrink away to nothing instead of falling, and since the action is most pronounced in the smallest drops, which are most curved, it is these smallest ones which chiefly disappear. Hence, when the pressure of vapour has risen so high that rain does begin, none of the drops are below a definite minimum size, because the smaller continue to feed the larger. If the air as a whole is

very damp indeed, however, the smallest drops, as they are first formed, may be able to persist, and then we have a "Scotch mist".

**FORMATION OF RAINDROPS.**—The formation of raindrops, by the way, even the smallest, is not the simple affair it might appear. The water vapour in the air does not merely condense here and there into liquid globules with no other cause than a fall of the temperature or pressure of the atmosphere. Aitken showed that centres or nuclei are necessary upon which the moisture may condense, and these are usually afforded by the dust particles always floating in the air. By careful removal of these motes by filtering the moist air through close-packed

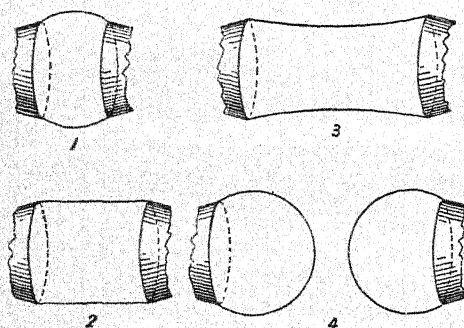


Fig. 81.—Soap Bubbles

cotton wool we can prevent condensation, so that the dust-free gas, contained in a glass vessel with a piston, may be expanded suddenly and so cooled several degrees, and yet still remain transparent and purely gaseous; whereas ordinary air in such circumstances would immediately become opaque by the formation of a dense fog of tiny water droplets. Later it will be seen

that electric charges may replace the dust, and act as condensation nuclei in moist air.

**SOAP BUBBLES.**—A soap bubble is a film of soap solution in which the forces of surface tension are so great compared with the weight that they are able to keep it in a sensibly spherical symmetrical shape without flattening or tendency to break.

A couple of small funnels, a short piece of rubber tube, and some soap solution, made of soft soap with a little glycerine, are all the apparatus necessary for a number of suggestive experiments with bubbles. Dip the wide end of a funnel into the liquid, remove it with a film across the opening, and blow this out into a bubble. Left to itself, with the narrow end of the funnel open, it shrinks up till there is just a flat film across the mouth again, and even then goes on contracting until the straight tube is reached. The film is evidently under tension. By applying the mouth of the second funnel to a bubble on the first, and slowly separating the two, we can draw the film out successively into the shapes of a barrel, a cylinder, and a spindle, and finally separate it into two bubbles.

The pressure inside a bubble is greater than that of the atmosphere



## THE BLACK SPOTS OF VERY THIN SOAP-FILMS

(By the kind permission of Mr. H. Stansfield)

Photographs 1 to 4 show successive stages in the thinning of a flat soap-film stretched on a frame of glass rods.

- 1, Moderately thin: coloured bands (Newton's rings).
- 2, Thinner film: the coloured bands more widely spaced; small black spots, too thin to reflect light, appearing at the top.
- 3, The black spots have coalesced to a black band across the top of the film.
- 4, The second thinner black spot appearing within the first black one. Observe the droplets of soap solution extruded at its edges.

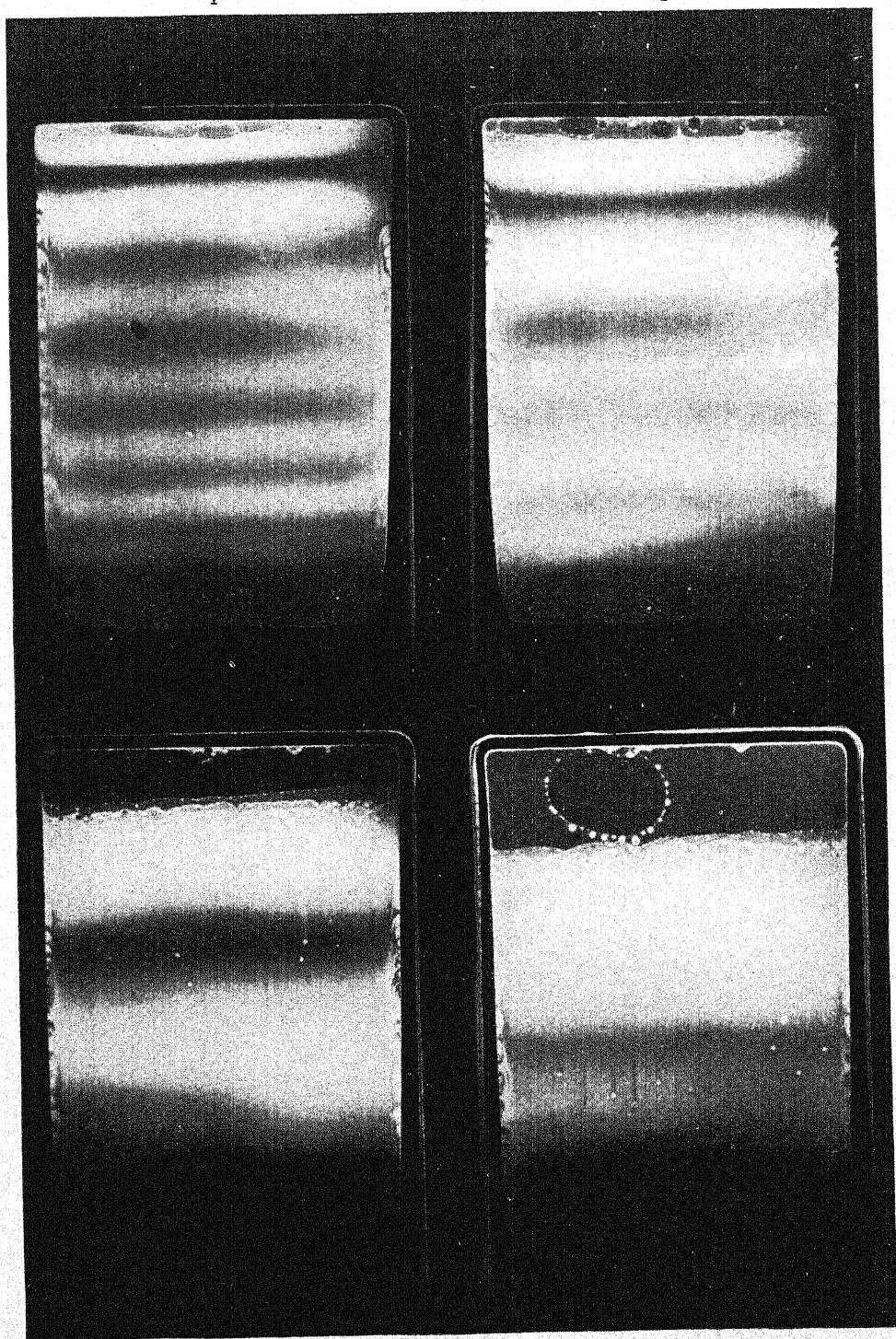
The film as a whole is in each case a little thicker at the bottom than at the top; the gradation is regular, as shown by the gradual changes from light to dark in the photographs of the coloured bands. Abrupt changes of thickness, however, occur at the boundaries of the black spots, causing their sharply marked appearance.



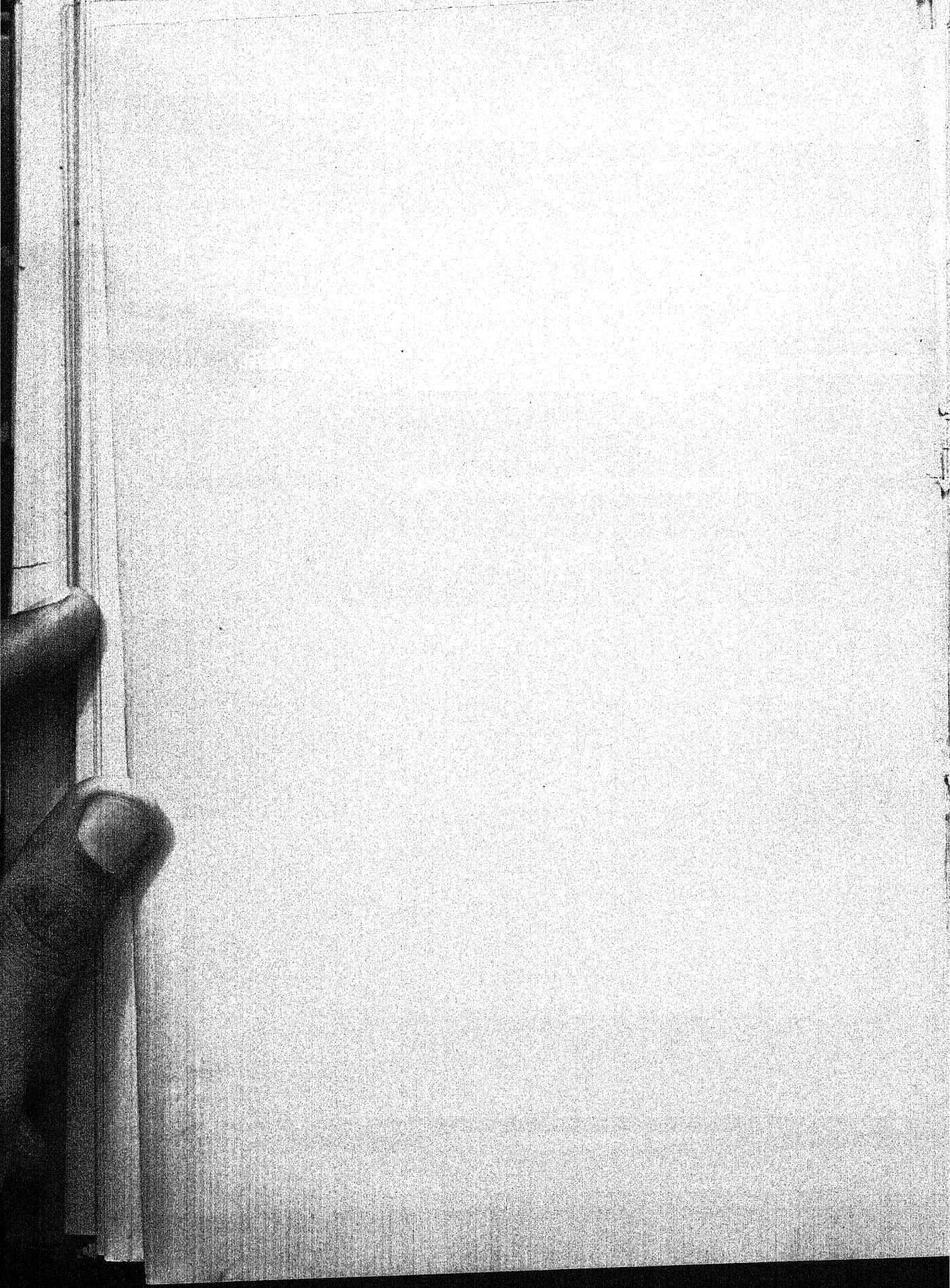


1

2



3 THE BLACK SPOTS OF VERY THIN SOAP-FILMS 4





without, as the shrinking of the bubble showed. A curious point is that the smaller the bubble the greater is this excess of pressure. Blow a bubble on each of the two funnels, one larger than the other, and then unite the small ends by a piece of rubber tubing; the greater pressure of the smaller bubble expels air from it, so it gradually shrinks, blowing the big one up to a greater size than before.

The surface tension of a solution is less than that of the pure solvent, as a general rule; hence if we throw small bits of camphor upon the surface of a tray of water, the camphor, never dissolving symmetrically all around, finds liquids of different surface tensions on the two sides of it. The greater tension on the less soluble side pulls the camphor about over the liquid. The particles, continuing this uneven solution, dart about like live things, often wheeling in spirals or circles faster and faster until they have quite dissolved away.

REMOVAL OF GREASE BY PETROL.—The removal of grease from cloth by petrol is a practical application of the same principle; the petrol is applied in a ring around the stain, and begins to dissolve it. Thus there are now two liquids—the grease solution and the pure petrol; the greater tension of the latter causes it to drive the grease into the middle of the ring, where blotting paper should be ready to receive it.

COLOURS OF THIN SOAP FILMS.—The study of the colours of thin soap films has led to an important calculation of the distances of molecules. When the film becomes only a few molecules thick, we should expect its properties to change considerably. This change is shown very clearly by the appearance of a black spot in the film, which careful measurements show to be thinner than the surrounding coloured parts, the thinning being sudden, not gradual. Within the black spot occur grey layers and a still thinner black spot, each thickness appearing suddenly. This series of disturbances all occurs at thicknesses less than about four-millionths of an inch, or  $10^{-5}$  cm. This, therefore, represents the upper limit of those distances which may be called molecular. Stansfield has succeeded in the delicate task of photographing the various black and grey patches, obtaining pictures of great beauty, of which four are here reproduced (see plate). Observe the tiny drops of surplus liquid expelled from the thinner black portions.

SOLUTIONS.—Solutions, especially such as those of a salt in water, lead us to new manifestations of molecular activity. It was long known that liquids could percolate through membranes, and Pfeffer showed that a solution of sugar in a tube closed at its lower end by such a membrane, and dipping into pure water, increased in amount: the pure water from

without entered the tube at a faster rate than the water of the solution could escape, while the membrane was altogether impermeable by sugar. Thus the height of liquid in the tube goes on increasing to a height of several feet before equilibrium is attained. This apparent diminution of the sugar solution pressure is known as the OSMOTIC PRESSURE between it and the water. Its physical explanation has been suggested to lie in the fact that there are proportionally fewer water molecules to bombard the membrane on the side where the sugar is, and so the pure water side gains on the other. This must in any case be an imperfect description, for it leaves out of account all influence of the membrane itself, which experiment shows to play an important part.

VITAL PROCESSES.—At the end of the long cells of plant stems are peculiar membranes, and it appears likely that osmosis here plays a part in sucking water up into the stem by the difference of pressure between it and the cell sap. In the lungs, again, osmosis aids in the absorption for purification of the vitiated blood.

VAN'T HOFF'S WORK ON OSMOSIS.—Van't Hoff, in a now-famous essay, showed that measurements of the osmotic pressure, and of the volume of a solution of a given quantity of a dissolved substance, proved that doubling the pressure halved the volume, just as though the substance were in the gaseous state filling the space of the solution, and so obeying Boyle's Law. The inference is not, of course, that we really turn the solid into a gas, but, what may after all not be so very different, that we have dispersed the solid's molecules through so large a space that they are about as far apart as gas molecules. A temporary check came when it was discovered that the osmotic pressures of such substances as common salt, copper sulphate, or the mineral acids were greater than they should have been on the gas analogy for the same number of molecules. This deviation from the behaviour of such substances as sugar was most marked in very dilute solutions. A brilliant surmise explained the difficulty: some of the molecules have split up into simpler parts, so that there are more particles roaming the fluid, and so giving what is practically a greater gas density. The theory, as first put forward by Clausius, supposed a certain fraction of the number of molecules to be permanently broken up, or dissociated as it is called. The awkward question instantly arises: What difference can there be between these and the molecules which do not divide? The later version of the theory therefore supposes that the impacts of the molecules of the substance upon the liquid molecules, and upon the walls of the vessel, break them all up in turn, but that they also tend to recombine when their scattered



members meet. The number dissociated at any instant is thus a floating population, always practically the same in number, though not composed of the same individuals; much as the number of travellers separated from their friends on ocean voyages may remain fairly fixed, through the balance struck between fresh partings as some ships sail and the reunions as others return.

Strong confirmation of the truth of this view is afforded by the phenomena of the conduction of electricity by these same solutions, or electrolysis, not only in the general form, but in the exact amount of dissociation required to explain the facts of experiment.

Thus the difference between these solutions and those of such substances as sugar is that in the latter case the molecules are roaming as wholes, while of those of salts and mineral acids some are divided up into two so-called ions (Gk., travellers). These consist, to take the instance of common salt, of the atoms of sodium and of chlorine, but electrical facts show that these are not plain atoms, but that the sodium is positively and the chlorine negatively charged with electricity. The proportion of dissociated molecules naturally increases as the solution is made more dilute, because the chances of a sodium ion meeting and pairing with a chlorine ion are lessened. Thus in extremely weak solutions all the molecules are broken up.

**COLLOIDS.**—An imperfectly understood class of solutions is that of the colloid or glue-like bodies. They do not pass through even such membranes as thin parchment, which is readily traversed by substances like the salts above discussed. They seem only to remain in solution when the dissolved substance is electrified, and, above all, they have the power of coagulating; under certain conditions. It seems possible that they are not true solutions, but a less intimate mixture of the colloid and the liquid, more of the nature of an emulsion. This "suspension" hypothesis is supported by the fact that, as well as the more ordinary colloidal bodies, albumen and the like, some metals (notably gold and silver) can be thrown into a similar state in water, for instance, by passing strong electric sparks between two wires of the required metal immersed under water. The intense discharge tears tiny particles from the wires, or perhaps momentarily vaporizes them, and the coloured solutions produced must, it would seem, carry at least some of the metal in suspension.

## CHAPTER IV

## HEAT

THEORIES OF HEAT.—The older theory that heat was a substance, CALORIC, which in some way inhabited matter in varying proportions according to its hotness, failed to explain how water, which incontestably contains more heat than ice, can yet be produced by rubbing two pieces of ice together. The newer theory which sprang from the reflections of physicists on this and similar experiments still holds the field, and has indeed become a certainty. Briefly it regards "Heat as a mode of Motion", to quote the title of Tyndall's classic work. By this is rather meant that what we term heat is a result of a mode of motion of the molecules of a substance, namely, the ENERGY with which that motion is associated.

GASES, LIQUIDS, AND SOLIDS.—Take the case of a gas, the flying molecules possess kinetic energy, and, if allowed to play upon a piston, can force it back against any pressure less than their own, thus doing work. If we heat the gas its pressure increases, showing that its molecules move faster; if we cool it the pressure drops, due to the slowing of the molecular speeds. Turning to liquids and solids, the effects of temperature can be similarly explained. Their expansions on heating, the increased fluidity of such viscous liquids as glycerine, such things are readily understood if we think of heat as an addition to the energy of motion of the molecules. A stage further, the melting of a solid or the boiling of a liquid by the application of heat must be expected if it produces this enhanced motion of the molecules, making their mutual gravitational attractions less and less important relatively to the violence of their collisions.

LATENT HEAT.—The act of freeing the solid's molecules from their rigid hold upon each other must need a certain amount of work to be done upon them, in other words, heat must be used up in merely melting the solid without raising its temperature; and that is just what we mean by the experimental *Laws of Fusion*, which tell us that while a substance is melting its temperature remains steady until all has liquefied, and that heat is spent in the process, the LATENT HEAT of fusion. This is as much in the case of water as would heat it from the summer air-temperature to the boiling-point. So again with boiling, the rending asunder of the molecules from their mutual attractions to set them in the widely scattered state represented by a gas or vapour; this must also need the expenditure of heat, and here again we find experimental agreement;



in turning water into steam, as much heat is needed as would raise the temperature of nearly five and a half times the weight of water from freezing- to boiling-point.

EXPANSION.—The expansion of nearly all substances when heated has just been commented on as a natural result of the increased molecular motion which heating implies. The molecules, moving to and fro more rapidly and therefore more vigorously, keep one another at a greater average distance apart by their repeated collisions. The expansion thus brought about should then be most marked in gases where mutual attractions between the molecules scarcely exist at all, less in liquids in which these forces are greater, and least of all in solids whose rigidity and resistance to compression indicate an almost perfect grip of molecule upon molecule. And so it is; iron expands only one three-hundredth part of its bulk when heated from the freezing-point to the boiling-point of water, quicksilver one-twentieth part, while air adds more than one-third to its bulk under the same circumstances.

Other gases, whatever their nature, expand to the same extent as air, and this also we should expect if heat is motion; for whatever the molecules may be, whether of oxygen, hydrogen, argon, carbonic acid, or any other gas, their collisions will be increased in the same degree by a fixed amount of heating, and there is no inter-molecular attraction in any of the gases to render its behaviour different from that of the rest.

Solids and liquids on the other hand show marked differences in their expansibilities; metals expand far more than such substances as stone, wood, or glass, and among the metals themselves there are differences. Tin expands more than brass, and brass more than iron. A few alloys are notable as exceptions from the fairly large expansions of metals; thus the nickel-steel alloy invar has already been alluded to as a valuable material for measuring tapes in surveying; its length hardly changes at all by the action of heat.

Unequally expansive metals are frequently used in the pendulums of accurate clocks; the bob in some is supported not by a single metal or wooden rod but by a sort of gridiron arrangement of steel and brass bars, joined together in such a way that the steel on expanding lengthens the framework while the more expansive but shorter brass lifts the bob to an equal amount, keeping the pendulum at a practically constant length. In other forms the bob itself is a jar of quicksilver. This when heated expands, and so its centre of gravity rises; by using the correct amount of the metal this rise can be made just to compensate the increase in the length of the supporting rod of the pendulum.

**FIRE ALARM.**—The diagram, fig. 82, shows a fire alarm consisting of a compound bar of two metals which by slight downward bending touches a metal point, completing an electric circuit and so ringing a bell. The upper side of the bar is made of more expansive metal than the lower, so that an outbreak of fire warming the bar bends it downwards as required and sounds the alarm.

**BALANCE WHEELS OF WATCHES.**—Balance wheels of watches are compensated for changes of temperature by a similar device. The expansion in warm weather of the radii, the spokes of the wheel, tends to make the watch run slow. So the rim is built up of three separate arcs, each, like the alarm bar above, made of two metals, and these bending inwards keep the mean diameter of the wheel and therefore also its quickness of vibration quite constant.

**FREEZING OF SOLUTIONS.**—Solutions of salts in water always freeze

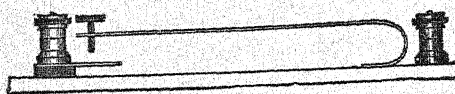


Fig. 82.—Fire Alarm

at lower temperatures than pure water itself; the lowering of the freezing-point is proportional to the amount of salt dissolved.

Further, the remarkable fact was observed by Ostwald that this depression per gram of a salt was inversely proportional to its molecular weight, *i.e.* directly proportional to the number of molecules. In other words, one molecule causes the same lowering whatever the dissolved substance is. There are two classes of bodies in each of which this is true; the one consists of such substances as sugar, alcohol, and glycerine; the other, the salts of the metals in dilute solutions. But in the latter class the depression is twice as great as in the former; thus there appear to be twice as many particles in the solution, a striking confirmation of the dissociation theory of solutions.

**FREEZING MIXTURES.**—Freezing mixtures depend on the fact that a certain amount of heat is required to dissolve most salts in water. Ice and salt, for instance, form a solution when the ice begins to melt, and the act of dissolving lowers the temperature of the mixture. The process goes on, and the freezing-point constantly gets lower as the solution grows in strength, until it becomes saturated. After this, further cooling is impossible, the lowest temperature reached being the freezing-point of the saturated solution; in the case quoted,  $-22^{\circ}\text{C}$ .

**BOILING-POINT.**—An exactly similar influence is exerted by dissolved substances upon the boiling-point of water, except that this time the point is raised instead of being depressed. The same doubling occurs in the case of the dissociable salts and acids.



**EVAPORATION.**—The process of evaporation consists in the darting of molecules away from the liquid surface into the air above; a certain number will also return in their zigzag flight through the vapour, but in general fewer return than leave. If evaporation goes on in a closed vessel, the number of molecules returning will eventually balance the number leaving the liquid. Then the air space above is "saturated" with the vapour; the process is quite similar to that of the solution of a solid in a liquid, when the same exchange goes on between the molecules dissolving and those already in the liquid, unequally at first, but eventually balanced when the solution is saturated. In either case a rise of temperature has its effect in aiding the evaporation or the solution as the case may be.

**EFFECT OF PRESSURE.**—Increased pressure tends to prevent the escape of the molecules from the liquid, so evaporation is checked. Thus the boiling-point of a liquid is raised by pressure. Water, which boils at  $100^{\circ}$  C. under an atmospheric pressure of 30 in. of mercury, only does so at  $101^{\circ}$  under 31 in., while 29 in. permit it to boil at  $99^{\circ}$ .

The effect of pressure upon freezing depends upon the substance; if, like wax, it expands on melting, added pressure tends to keep it solid, and so raises the freezing-point. If, on the other hand, it contracts on melting, like ice, pressure helps the change into the liquid state, and the freezing-point is lowered. Type metal owes its good clear-cut appearance to a similar expansion on solidifying, and iron makes excellent castings for the same reason.

**ICE AND WATER.**—The fact that ice is lighter than water is of extraordinary significance. If ice sank on freezing, forming layers at the bottoms of ponds and streams, and eventually of the sea, it would take a very long time to melt again on the return of spring. The temperature of the whole globe would fall, winters would become longer, while the heat which now melts the surface ice would be employed in evaporating water, and would further profoundly affect climate. The effect, too, of the expansion during frost in breaking up and "fining" the soil is well known to farmers and gardeners.

**CONDUCTION.**—The passage of heat from one part of a body to another by conduction is another instance of the energy of the molecules. In the case of a gas it can be shown by passing an electric current through a wire or carbon filament in a vacuum, making the current just strong enough to cause the filament to glow brightly. If air is gradually admitted to the wire the glow becomes dimmer and dimmer, and may cease altogether when the air is at full pressure. The heat is led away through

the gas, and so the wire grows colder. This conduction it is that makes the electric glow lamp safe in fiery mines. If the bulb is broken, and the explosive gases are admitted to the hot carbon, they conduct off its heat too rapidly for themselves ever to reach their "flash-point", and the filament soon burns away in the air, stopping the current altogether.

In the case of a solid, one might expect very poor conducting qualities, because of the relative immobility of the molecules. On the contrary we find that solids really conduct heat very much better than any gas or liquid, thousands of times better in the case of some of the metals. It had become the custom to explain this by the supposition that heat applied at one end of the bar set the molecules there into more violent motion than usual, something of the nature of vibrations of an irregular kind. This motion was passed on from molecule to molecule through the substance by a sort of wave motion. This action must certainly go on to some extent, but no particular relation exists between the elastic properties and the conducting power of a substance, such as we might expect if this were the whole of the matter.

**ELECTRONS.**—The ubiquitous electron, about which we shall have so much to say later, here plays a part. For our present purpose, an electron is a tiny detached part of an atom, and such parts exist in great numbers in solid bodies, especially in metals. On account of their small size the electrons are free to roam about in the chinks between the atoms, and especially through the atoms themselves, with as little restraint and as few collisions as a gas molecule. Further, they travel with far higher speeds on account of their minute mass, and so will be far more effective in carrying heat than the clumsier molecules. Good conductors of electricity are always good conductors of heat, a remarkable corroboration of this theory that the carriers of the energy that we know as heat are the electrons, which are also the vehicles of the electric current.

**HEAT EQUIVALENTS—Joule's RESEARCHES.**—Now if heat and energy are two names for the same thing, a quantity of heat ought to be expressible in work units as so many foot-pounds or so many horsepower-hours; is this so? Joule, in 1843 and onwards, performed experiments which answered the question with an emphatic "Yes". His experiment is too well known to need any detailed account. Briefly, he stirred water, and measuring both the work expended and the heat produced by the friction in the water, found that the ratio of the two was always the same, and so expressed heat units in foot-pounds. The calculation is exactly parallel to the process of measuring the length of a line in inches and in centimetres, and so finding the number of centi-



metres in an inch. His conclusion was that 1 unit of heat was equal to 778 ft.-lb., the HEAT-UNIT being the amount required to raise the temperature of 1 lb. of water by 1° F. Expressed in the units of the metric system, the relation is that the CALORIE is equal to  $4.2 \times 10^7$  ergs. Numerous experiments, conducted along various lines, have confirmed the truth of this result. Electric currents of known power, the measured work done by a gas in expanding, the stirring of other liquids such as mercury, and several other devices have been used to produce the heat, and the same figures have always been obtained for this relation, the MECHANICAL EQUIVALENT OF HEAT. The importance of this measurement can hardly be overestimated. The modern development of steam and other heat engines has proceeded entirely along lines indicated by the possibility of exactly determining the quantity of work which, under specified conditions, can possibly be obtained from the transformation of some heated body, the expansion or contraction of steam, or the explosion of mixed gases.

Here we have the promised extension of the law of the conservation of energy to include the cases when work has apparently disappeared, for instance, in the stopping of a bullet by a target. The kinetic energy of the flying bullet has passed into the form of heat, to an equivalent amount.

The science of THERMODYNAMICS, without knowledge of which no engineer can hope to effect any great progress, takes this equivalence of heat and work as its FIRST LAW.

DISSIPATION OF ENERGY.—The SECOND LAW is of hardly less importance; founded, like the first, entirely upon experience, it states the impossibility of getting useful work out of a body by cooling it below the temperature of the coldest of its surroundings.

From this follows what is known as the principle of the dissipation of energy, that all forms of energy tend ultimately to pass into the form of heat, and so, by the physical processes of conduction or otherwise, to become unavailable. The universe thus tends to lose its useful energy by this degradation into heat, and the second law tells us that the energy is ultimately irrecoverable. The world must finally arrive at a state of uniform temperature, when all ordinary activities must cease. The earth will gradually slow down in its rotation until it always presents the same hemisphere towards the sun, as the moon does now towards us. Our yearly revolution will also slow down, and the earth will be drawn inwards, to fall at last upon the sun. It will cause new evolution of heat in its impact, but the process must still

continue until the entire universe has lost its motion. We can only escape this conclusion of a finite term of life for the world by supposing that somewhere in space there may be a building-up process at work, supplying new energy without the restrictions of the second law, but of this we have at present no particle of evidence.

ABSOLUTE LOWER LIMIT OF TEMPERATURE.—If heat is motion, there should be a real lower limit to temperature, an absolute zero, viz. that at which all molecular activities cease. Many ordinary chemical and physical actions are affected by changes of temperature, and grow less in intensity or rate of progress when bodies are cooled. Thus, to take at once extreme cases of cold, a photographic plate is only one-fifth as sensitive at the temperature of liquid air as it is under everyday conditions. The electrical resistance of a metal diminishes rapidly as it is cooled, and at the temperature of liquid hydrogen copper conducts 100 times as well as at ordinary temperatures. Such properties as those of magnetization, which are interfered with and lessened by molecular motions, on the other hand, show remarkable increases at these very low temperatures, because the motions are checked by the extreme cold.

SUSPENDED ANIMATION OF LIFE.—However, it may here be noted that bacteria, the organisms which set up putrefaction in meat, and some seeds such as peas, can be exposed to these intense refrigerations for hours or days, and yet, on being thawed, resume their usual life functions with unimpaired vitality. If, then, as seems possible, matter can be projected at all from one planet to another, there seems no reason why living matter should not be thus projected in a state of suspended animation, to revive and multiply in its new home.

EXTREME COLD.—To return to our story, it appears possible from many phenomena to reduce the molecules of substances to rest by extreme cold; in fact, on our work-theory of heat, extreme cold means the same thing as diminished motion. A simple case is that of the contraction of gases; all diminish in volume by about  $\frac{1}{273}$ rd part for each degree Centigrade that they are cooled, so if we could continue the process down to 273 degrees below the freezing-point, the volume would be nothing, or rather the molecules would have shrunk into absolute contact. (In reality, of course, such nearness would necessitate liquefaction and then solidification at certain stages of the contraction.) A gas thermometer, then, one in which the expansive substance was air or hydrogen instead of quicksilver, would have an absolute zero of  $-273^{\circ}$  C.



**WORK THERMOMETER.**—The air thermometer depends on the properties of a gas, but Lord Kelvin was able to devise a scale of temperature which is absolutely independent of the working substance, being based entirely on thermodynamic principles. This is the **WORK SCALE**, in which the degree is the difference of temperature which must exist between the source and the refrigerator of a perfect engine for the performance of a certain fixed amount of work per stroke. The particular size of the degree depends, of course, upon the quantity of work chosen, and, using the Centigrade degree for convenience, Lord Kelvin found that the work scale agreed almost exactly with that of a gas thermometer, not only for the particular point from which the size of the degree was borrowed, but also for extreme ranges either of heat or of cold. So the absolute zero again proves to be  $-273^{\circ}$  C. The meaning of the agreement between the gas thermometer and work thermometer scales is that the same amount of energy has to be supplied to a mass of gas to produce a given expansion at all parts of the scale.

**RADIATION.**—An aspect of heat which has received a good deal of attention in recent years is that of radiation by hot bodies. The familiar experiments of the focusing of heat from the sun by a lens or burning glass, or the ignition of phosphorus at the focus of one concave mirror by the radiation of a red-hot iron ball placed at the focus of a second, prove that heat can be radiated, reflected, and refracted much as light, and there remains no doubt that such heat radiations pass through space by ether waves identical with those of light, except that the wave lengths are somewhat greater. If we examine the spectrum thrown by a prism by means of a very delicate thermometer (such as a thermo-couple or a radiometer, p. 183), we find that the heating effect grows as we pass from the blue end towards the red, does not stop with the luminous rays, but goes on increasing into the dark region outside the red end, reaching a maximum in this "infra-red" region, and then dies away again. Analysis of their properties shows that these dark heat waves are of lengths ranging from rather less than  $\frac{1}{100000}$  inch up to nearly  $\frac{1}{1000}$  in., or 100 times as long. Light waves range from the shorter limit mentioned as their longest form up to roughly half that length (in the violet of the spectrum), a far shorter range. The eye is only sensitive then to a very limited series of ether waves.

**STAGES OF HEATING.**—As a body is heated, the radiations which it emits do not remain of the same wave length, but vary through constantly widening limits. Iron, for instance, when only "black-hot", emits no waves shorter than  $\frac{1}{100000}$  in., but as its temperature rises, shorter and

shorter waves appear, until the iron begins to shine with the longest visible waves, and the red-hot stage is reached. Next the yellow is added, and so, in order, all the other rays of the spectrum, until the metal glows white.

APPARENT HEAT RADIATION.—A body radiates heat by means of the vibrations of its molecules and atoms, or of the electrons within its atoms. Vibrations need energy for their maintenance, and fritter that energy away either directly as heat in the spreading of the vibrations through the substance, *i.e.* in conduction, or by sending out a train of waves. Such radiation from a vibrating body is exemplified in the case of the sound waves set up by the swinging prongs of a tuning fork. Here again, too, waves of another kind are flung out through the ether by the vibrating atoms or electrons. To produce these heat waves the vibrations must go on at the rate of about 300 billions per second. Energy is carried in the waves, but not heat in any ordinary sense of the word; when, however, such waves fall upon any body whose particles are free to be set into similar motion by the "shake" of the waves, then heat will be manifested in this body, and we have the apparent radiation of heat.

So if we take a can of hot water, its radiations will melt a piece of ice put near it; but if we put a red-hot ball in place of the ice, the ball radiates heat to the can. Why, we ask, has the hot water stopped radiating merely because its environment is changed? The answer is simple. It has not ceased to radiate, nor have its radiations even grown feebler, but the red-hot ball emits waves more strongly, so that the can receives more than it gives. So also the ice radiated, but less powerfully than the can, which therefore on the whole lost heat. The coolings and heatings by radiation that we perceive are in all cases merely difference effects, the balance of credit and debit columns.

Every substance that has moving molecules, everything that is above the absolute zero, radiates energy, and its radiations grow stronger as its temperature rises. The exact manner of this increase with temperature has been the subject of much investigation, and Stefan at last showed experimentally what has since been deduced from thermodynamic theory, that the radiation of a given body varies approximately as the fourth power of its absolute temperature, *i.e.* its temperature as measured from  $-273^{\circ}\text{C}$ . So the radiation from water at its boiling-point is three and a half times as great as when it is at the freezing-point. The law is only exactly true in the case of a "perfectly black body", that is, a substance which absorbs every wave which falls upon it, reflecting none.



**STEFAN'S LAW OF RADIATION.**—Stefan's law of radiation has been applied to calculate the temperature of the sun. We can measure the heat radiated in sunshine to the earth per square inch at our known distance from the sun. From this the whole amount radiated in all directions is calculated, giving the amount per square inch of the surface of the sun by another simple calculation. To deduce the temperature which corresponds to this rate of emission of heat, we need to know whether the surface of the sun is similar to that of the radiating bodies we are familiar with upon the earth. For a black substance at a given temperature radiates more than a bright one, and every difference in surface causes a change in emission. But even though we do not know exactly whether the sun behaves as a black or a metallic body, we can make an approximate estimate of his temperature, and the latest measurements point to something between  $5000^{\circ}$  and  $7000^{\circ}$  C. as the most probable limits.

The methods by which heat radiations can be detected and measured afford a record of brilliant experimental progress.

**CROOKES'S RADIOMETER.**—Crookes's radiometer, the familiar toy of opticians' windows, consists of a lightly pivoted system of vanes, black upon one side, polished metal upon the other, in a glass tube from which the air has been as far as possible exhausted. Heat falling upon the vanes is absorbed almost entirely by the blackened surfaces, but is largely reflected by the bright ones. The black faces thus reach the higher temperature of the two, and the greater energy they radiate increases the violence of the impact upon them of the few gas molecules left in the bulb. Thus the pressure upon the darkened sides exceeds that upon the others, and the little mill revolves, bright faces in front. The high vacuum is needed to prevent equalization by the conduction of heat through the air, and to reduce resistance to the motion. Ordinary sunlight thus sets the vanes whirling merrily, and any sufficiently hot body will do the same.

**THERMO-PILE.**—A sensitive measuring apparatus is the ordinary thermo-pile. If two wires of different substances are joined at each end so as to make a complete circuit, then the heating of one of the junctions of the two metals produces an electric current round the wires. The thermo-pile is a "battery" made up of a number of such wires, so that, for instance, the circuit might be made up of the series bismuth, antimony, bismuth, antimony, and so on, for a great number of pairs, the end of the system being connected to a sensitive galvanometer or other apparatus for registering the flow of a current through the wires. The bismuth-antimony

couples are made up into a sort of cube, with every other junction on one of the faces, the alternate ones on the opposite face. In this way one face can be heated by the radiations from any hot body, and the thermo-currents produced all act together in affecting the galvanometer.

**RADIO-MICROMETER.**—The comparatively large bulk and slow heating of such an instrument are drawbacks to its use in such delicate work as that of testing the relative heating powers of the different parts of the spectrum, and we cannot get over the difficulty by using only one or a few pairs of metals, because then the current through an ordinary galvanometer would be too small to be accurately observed. Boys, however, has surmounted this obstacle in the most ingenious way in the **RADIO-MICROMETER**, in which a single pair of metal strips, very small and light, not only form the whole circuit, but act as their own galvanometer. The tiny circuit of the two metals has one of its junctions made by a minute piece of blackened copper foil, and this receives the radiations to be measured, which heat the junction. The whole loop of metals only weighs half a grain, and is suspended between the poles of a powerful magnet. When the radiations fall on the copper, thermo-currents traverse the loop, and it is deflected by the magnet. The deflections are measured by the motion of a spot of light reflected from a small mirror attached to the circuit. That the twisting may be large, the apparatus is suspended by a Boys' quartz fibre as fine as can be procured. By the radio-micrometer the effect of a candle 3 miles away, focused on the copper foil by a telescope, can be distinctly observed, while the radiation from the moon is far too strong to be measured without some device for reducing the intensity of its light 1000 times or more.

**HIGH TEMPERATURES.**—Another fascinating line of research is that relating to the production and measurement of extremely high and extremely low temperatures.

The electric furnace, that is a vessel of refractory material inside which plays the flame of an electric arc, has been brought to a high degree of perfection in a long series of improvements and modifications by M. Moissan and others.

One important advantage of such heating is that high temperature can be applied just where it is required, in the heart of a powder to be heated, for instance, so that the full effect is obtained, and trouble from impurities contained in the furnace walls is avoided. Even when the electric current has to be produced by dynamos driven by steam power, these advantages may be sufficient to justify electrical methods; but it is in the case of cheap water power, such as that of Niagara, that the electric furnace has



reached its greatest practical value. To take two cases out of many, graphite can be produced electrically of greater purity than in the natural state, and the extremely hard, abrasive, and refractory material known as carborundum is entirely manufactured by electric furnaces.

In the GRAPHITE PROCESSES anthracite or coke, mixed with a small amount of other substances, is heated in the furnaces, and the ultimate form of the carbon remaining is graphitic.

CARBORUNDUM, which is a carbide of silicon, is obtained also at Niagara by more powerful electric heating of a mixture of sand and coke surrounding a central coke core. The oxygen of the sand burns off with some of the carbon from the molten mass, and carborundum crystals are left where the heating was most intense. The current, applied at 1000 horse power per furnace, passes directly through the coke core for thirty-six hours, and produces more than 3 tons of the crystals.

Phosphorus, iron, glass, calcium carbide, magnesia, alundum (another abrasive), and aluminium are among other products of electric heating.

PYROMETERS.—Such high temperatures as those of furnaces evidently cannot be measured by ordinary glass thermometers, and various PYROMETERS have been devised to meet the difficulty. Not only do most substances fuse at these high temperatures, but even the more refractory then permit gases to leak through their substance, so that the air or hydrogen thermometer is unavailable. Trouton, however, has recently held out hopes that he may soon perfect a kind of porcelain which is quite gas-proof even in the fiercest furnace.

BERTHELOT'S APPARATUS.—The precision of the gas thermometer is secured in an apparatus by Berthelot which measures the changes in the refraction of light in air heated to the required temperature. These changes go on quite proportionately to the decrease of density, and the latter is dependent simply on the absolute temperature; thus no leak in the air vessel can vitiate the results.

Another method is to heat a small black body in the flame, and to observe its radiation by a radio-micrometer or similar instrument, thence calculating its temperature by a method akin to that by which the temperature of the sun is estimated.

OPTICAL PYROMETERS.—Sometimes only one particular kind of radiation is observed, say the amount of red light emitted, and similar calculations are based upon that. The ideal at which such "optical pyrometers" aim has been well expressed by Sir Oliver Lodge as "estimating the temperature of a body by looking at it", but at present the theory upon which calculations are made is somewhat uncertain, and the work

of Holborn, Féry, and others is rather concerned with finding the most promising method than with actual exact measurements.

**EXTREME COLD.**—Some of the properties produced or affected by extreme cold have already been touched upon. The great refrigerations under which these studies have been made are produced entirely by improved processes for cooling gases by their own expansions.

**DEWAR'S RESEARCHES.**—One of the chief is that employed by Dewar in his celebrated researches at the Royal Institution. When a gas under pressure expands into the atmosphere it does work in driving back the

air, and the work has to come from its own energy, and therefore results in a fall of temperature. Dewar employs this fact in his apparatus, in which the cooled gas, after its expansion, circulates round the tube in which succeeding portions are flowing before their expansion. Hence the gas which is actually expanding becomes cooler and cooler as time proceeds, until the point of liquefaction is attained.

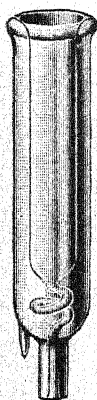


Fig. 83.—Vacuum-jacketed Vessel

**STORAGE OF LIQUEFIED GASES.**—The vessels employed to store the liquefied gases are double or treble walled, as shown, the outer jackets being evacuated (fig. 83). In this way the liquid is screened as far as possible from gain of heat by conduction through the air around. Silvering the outer surface lessens the absorption of heat, and still further decreases the rate of evaporation of the liquefied gas.

**LINDE'S METHOD.**—Another method—Linde's—utilizes the fact that no real gas is perfect, that is to say, in none are the molecules so far apart as to lie quite beyond each other's attractions. Consequently, even when a gas expands into vacuum, it does work in pulling its own molecules farther apart, and therefore becomes cooler. In Dewar's apparatus the expanded gas before liquefaction sets in escapes into the air after cooling the next portion, but in Linde's machines the same amount of gas is pumped round and round, each part cooling itself at each expansion, and cooling the remainder, as in Dewar's apparatus, after expansion. Thus the temperature of the whole amount steadily falls, until at last drops of the liquid appear and are collected in a suitable vessel at the bottom of the apparatus.

**HYDROGEN-GAS THERMOMETER.**—Low temperatures can be measured by the hydrogen-gas thermometer down to the point of liquefaction of air or thereabouts, but the errors rapidly increase about 230 degrees below zero, as the liquefaction of the hydrogen approaches. Helium, which has not yet been liquefied, obeys the gaseous laws, and can be used for ther-



mometry to yet lower temperatures, probably to 17 or 20 degrees absolute, some 250 degrees below zero.

**PLATINUM THERMOMETER.**—A thermometer which combines a very wide range of usefulness with extreme accuracy and sensitiveness is the platinum thermometer perfected by Callendar. Inside a tube made of refractory material, such as porcelain, is placed a length of fine platinum wire. Platinum (like most other metals) changes its resistance to the passage of an electric current when it is heated or cooled, and this quite regularly; the higher the temperature the greater the resistance. Hence

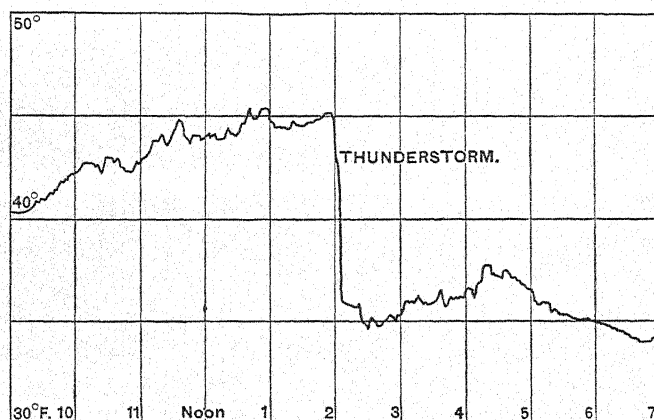


Fig. 84.—Temperature Chart

for any particular specimen of wire all that we need to do is once for all to find the resistance at a few specified known temperatures (say those of melting ice, boiling water, and boiling sulphur). The thermometer is then "calibrated", and at any subsequent time a measurement of its resistance gives the temperature of the wire. The thermometer is often supplied with a self-registering apparatus consisting of a galvanometer the motion of whose pointer indicates the changes of resistance, and so indirectly the changes of temperature. This pointer is in reality a light pen which traces its movements in ink across the width of a roll of paper. The paper is moved steadily lengthwise by clockwork, so an irregular wavy trace maps out the pointer readings at successive instants. Suitable division of the paper gives the temperature directly in Centigrade degrees. The annexed chart (fig. 84), shows the form of curve traced out, and illustrates the sharp fall of temperature occurring during a thunderstorm.

[Article on "Physics" continued in next volume.]